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## FINAL REPORT

### DESTRUCTION OF PROBLEMATIC AIRBORNE CONTAMINANTS BY HYDROGEN REDUCTION USING A CATALYTICALLY ACTIVE, REGENERABLE SORBENT (CARS)

July 1993

Prepared by:

John O. Thompson

James R. Akse

Contract Number: NAS2-13714

Ames Research Center

National Aeronautics & Space Administration

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(NASA-CR-194354) DESTRUCTION OF  
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## PROGRAM OVERVIEW

In future NASA missions, the TCCS will need to operate more efficiently over longer time periods with the use of fewer expendables due to the increased demands of larger crews and longer mission durations. The Space Station Freedom (SSF) baseline air regeneration system, a combination of carbon sorbents and a catalytic oxidation system, uses non-regenerable sorbent beds and an oxidation catalyst which is run constantly and is susceptible to poisoning by halogen, sulfur, and silicon containing compounds. The resupply penalties and energy demands of this system are high. Significant savings in both areas can be realized by the use of regenerable sorbents which specifically eliminate catalyst poisons allowing more efficient operation conditions to be used by the catalytic oxidizer.

A Catalytically Active Regenerable Sorbent (CARS) system is an air purification process which uses a sorbent bed composed of an activated carbon made catalytically active by metals dispersed on its surface. The same bed can be used as the sorbent, and during regeneration, as the catalytic reactor. A properly designed regenerable bed's sorption capacity is also adjustable since the timing of the regeneration cycle in a parallel bed system can be continuously adjusted to always adsorb the contaminant load.

The feasibility of a Catalytically Active Regenerable Sorbent (CARS) system has been demonstrated in this study. A complete adsorption and regeneration test performed on the best CARS combination clearly illustrates the effectiveness of this technology for the treatment of halogen and sulfur containing contaminants. The challenge mixture contained Freon-113, trichloroethylene, bromotrifluoromethane, and dichloromethane at 436%, 15000%, 11.2%, and 95.6% of their Spacecraft Maximum Allowable Concentration (SMAC) respectively as well as thiophene, a generalized organosulfur compound without a SMAC value. Approximately 100 liters of this challenge stream was sorbed by a 7.8 cm<sup>3</sup> bed before breakthrough occurred. The bed was then purged, filled with hydrogen, and heated to 250 C for 500 minutes followed by 300 C for 1100 minutes. After the initial heating, none of the original sorbed contaminants were detected demonstrating the high catalytic hydrogenation activity at these low temperatures. The multi-step hydrogenation of the remaining by-products required an additional 1600 minutes completing the regeneration. The CARS bed was then serviceable for a new adsorption run. The regeneration duration can be reduced considerably using higher hydrogen pressures and reactor temperatures, or by improvements in the catalyst.

Before the CARS approach to remediation of problematic trace airborne contaminants can be used to replace expendable sorbent beds in the current TCCS configuration, additional work is needed in several areas. Future work will involve challenging a CARS bed with a mixed contaminant stream representative of all classes of compounds in the TCCS model. The use of layered thermally desorbable sorbents must be investigated to optimize the sorption capacity of the bed for a mixed contaminant stream, and the effect of additional contaminants on catalytic hydrogenation must be determined. Optimization of the catalyst's activity and regeneration conditions will lead to a more efficient system, including the use of metal hydrides to initially provide and later scavenge unreacted hydrogen when a regeneration is complete. Evaluation and optimization of the alkanes produced during regeneration will allow the catalytic oxidizer to operate at lower temperatures. The impact of a fully developed CARS system on TCCS operation will include lower resupply penalties, greater flexibility in handling contamination events, lower overall system weight, and possibly lower energy consumption.

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## 1.0 INTRODUCTION

In future NASA missions, the TCCS will need to operate more efficiently over longer time periods with the use of fewer expendables due to the increased demands of larger crews and longer mission durations. The Space Station Freedom (SSF) baseline air regeneration system, a combination of carbon sorbents and a catalytic oxidation system, uses non-regenerable sorbent beds and an oxidation catalyst which is run constantly and is susceptible to poisoning by halogen, sulfur, and silicon containing compounds.<sup>1-4</sup> By using a process in which the sorbent beds are regenerated, while at the same time reducing the operating time and exposure of the catalytic oxidizer to catalyst poisons, resupply penalties and energy demand can be significantly reduced. A Catalytically Active Regenerable Sorbents (CARS) system is an air purification process using a sorbent bed composed of an activated carbon made catalytically active by metals dispersed on its surface. The same bed can be used as the sorbent and the catalytic reactor. While a non-regenerable sorbent bed will be limited in its sorption capacity to the least retained contaminant present in the air stream, a properly designed regenerable bed's sorption capacity is unlimited in the sense that the regeneration cycle for a parallel bed system can be continuously adjusted to always adsorb the contaminant load.

The catalytic regeneration is performed by purging the sorbent bed of oxygen with an inert gas, then filling and maintaining pressure in the regeneration loop with hydrogen. The catalyst bed is heated to operating temperature, 200 to 300 degrees C, while a pump circulates hydrogen through the closed regeneration loop. A lithium hydroxide bed contained in the regeneration loop scrubs the stream of volatile acid gases produced from halogen reduction. When regeneration is complete, hydrogen and alkanes, the only compounds remaining in the gas stream, may be purged from the sorbent bed and incinerated by the catalytic oxidizer. Operated in conjunction with a CARS system, the catalytic oxidizer can be operated more efficiently since its influent is more consistent and contains no catalyst poisons.

To determine the effectiveness of this air regeneration process, UMPQUA tested catalysts prepared on activated carbon supports containing combinations of nickel, molybdenum, palladium, ruthenium, and platinum to determine their relative effectiveness at reducing halogenated organic compounds. In order to test the CARS concept a model contaminant mixture containing dichloromethane, bromotrifluoromethane, trichloroethylene, thiophene, and Freon-113 was developed after consultation with NASA AMES personnel. The more active catalysts reduced these contaminants individually to alkanes at temperatures ranging from 125 to 200 C.

A comparison of the adsorption capacity of the catalyst to that of untreated activated carbon revealed minor losses of sorption capacity due to the deposited metals (Table 1). This retention of sorptive capacity allows the catalyst to also be used as a major component in the adsorption bed. If needed, other thermally desorbable sorbents can be added to enhance the sorbent bed's capacity.

Since the baseline catalyst was capable of reducing all of the contaminants chosen for this project and also function as an effective sorbent, the test stand's final configuration was developed (Figure 1). The test stand operates in two distinct modes: an adsorption cycle and a catalytic regeneration cycle. In the adsorption cycle, contaminated air passes through a sorbent bed composed of a mixture of 4 cc of the baseline catalyst and 4 cc of a Carbosieve, a component necessary to retain the most volatile contaminant, bromotrifluoromethane. A hydrocarbon analyzer monitors the effluent gas for contaminant breakthrough. In the catalytic regeneration cycle, oxygen is purged from the regeneration loop by nitrogen, which is in turn purged by hydrogen. The regeneration loop is then pressurized and maintained at 14 psig with hydrogen. A pump recirculates hydrogen through the catalyst bed while it is heated to the hydrogenation temperature. The catalytic hydrogenation of the halogenated contaminants produces acid gases which are released into the recirculation loop where a room temperature lithium hydroxide bed removes them.

The baseline catalyst; 5%Ru, 20%Pt on activated carbon; was run four times with various contaminant concentrations and regeneration temperatures. Due to time constraints, total regeneration of the bed by destruction of all contaminants was not performed.

The test stand was run with a catalyst containing 5%Ru, 20%Pt, and 10%Mo. The bed was initially loaded with contaminants to saturation, as indicated by the breakthrough of bromotrifluoromethane. Total regeneration of this bed was performed in a timely manner demonstrating the CARS concept. This catalyst showed a much greater activity for reduction of the contaminants compared to the baseline catalyst.

## **2.0 SELECTION OF MODEL CONTAMINANTS**

URC collaborated with NASA AMES personnel to select five contaminants which are potential catalyst poisons for the TCCS catalytic oxidizer: Freon-113 ( $\text{Cl}_2\text{FC}-\text{CF}_2\text{Cl}$ ), the most abundant contaminant in the TCCS model; dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and bromotrifluoromethane ( $\text{CBrF}_3$ ), two other contaminants found in the TCCS model; trichloroethylene ( $\text{HCIC}=\text{CCl}_2$ ), a common industrial solvent; and thiophene, a contaminant

SORBENT MATERIAL	COLUMN SIZE	CONTAMINANT	CONCENTRATION mg/L	SORPTION mg/cc	FLOW RATE
Activated Carbon	6cc	Freon 113	8.15	300	1370
5%Ru, 20%Pt Catalyst	6cc	Freon 113	8.15	235	1370
Activated Carbon	4cc	Freon 113	0.475	122	650
5%Ru, 20%Pt Catalyst	4cc	Freon 113	0.49	107	650
Activated Carbon	4cc	CH <sub>2</sub> Cl <sub>2</sub>	0.168	11.6	650
5%Ru, 20%Pt Catalyst	4cc	CH <sub>2</sub> Cl <sub>2</sub>	0.198	13.7	660
5%Ru, 20%Pt Catalyst	4cc	Thiophene	0.43	122	860
5%Ru, 20%Pt Catalyst	4cc	TCE	1.78	274	770
5%Ru, 20%Pt Catalyst	4cc	CBrF <sub>3</sub>	0.35	1.9	710
Activated Carbon	4cc	CBrF <sub>3</sub>	0.35	1.9	710
ACF-1605 Cloth	2cc .45gm	CBrF <sub>3</sub>	0.35	1.6	710
Carbosieve S-III	4cc	CBrF <sub>3</sub>	0.35	13.6	680

Table 1. Single Contaminant Adsorption Results



# CARS Adsorption/Recirculating Catalytic Hydrogenation Test System

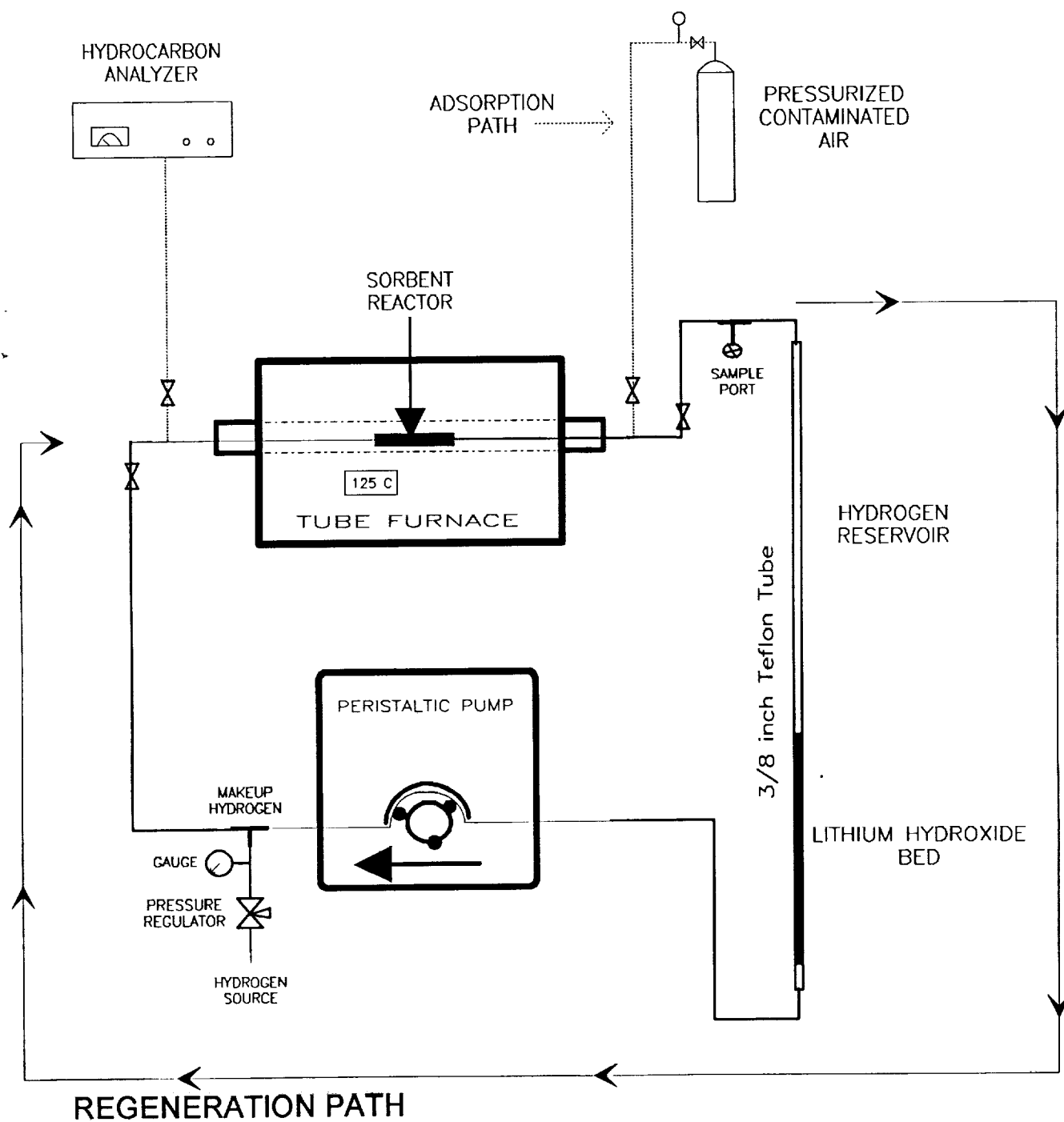


Figure 1. Final Test Stand Configuration

representing organosulfur sources particularly problematic for oxidation catalysts. The following table is provided for comparison purposes<sup>1</sup>. The third column contains a calculated generation rate of contaminants for a 4 module space station with 31500 cubic feet of air assuming that no air purification occurs over a period of 24 hours.

CONTAMINANT	SMAC mg/Liter	GENERATION RATE SSF AIR VOLUME mg/day Liter
Bromotrifluoromethane	0.6088	0.00052
Dichloromethane	0.0868	0.00193
Freon-113	0.383	0.0254
Thiophene	-----	-----
Trichloroethylene	0.00054	0.000044

**Table 2. Contaminant Generation Rates and SMAC Limits**

### 3.0 ADSORPTION AND DESORPTION STUDIES

#### 3.1 Single Component Adsorption Study

To determine the system's final configuration, a comparison between sorption capacities of the baseline catalyst and its untreated activated carbon substrate was established (Table 1). If the carbon substrate's sorption capacity were significantly reduced by the addition of catalytically active metals, another bed would be needed to trap and then thermally desorb contaminants during regeneration into the catalytic reactor. If the sorption capacity were not significantly reduced, the same bed could be used as both a sorbent and a catalyst.

The sorption comparison between the baseline catalyst and the activated carbon was established at two concentrations of Freon-113 and one concentration each of dichloromethane and bromotrifluoromethane. At the high concentration of Freon-113 (8.15 mg/L = 8150 mg/m<sup>3</sup>), the catalyst adsorbed only 78% of the untreated carbon's capacity. However, at a lower concentration of 0.48 mg/L, the catalyst adsorbed 88% of the untreated carbon's capacity. For the concentrations of dichloromethane (0.168-0.198 mg/L) and bromotrifluoromethane (0.35 mg/L), the catalyst adsorbed the same amount as the untreated carbon. The reason for the catalyst's loss of sorptive capacity with respect to Freon-113 is

uncertain, but the loss is limited at lower concentrations, which are closer to the TCCS model. The limited loss of sorptive capacity due to the addition of catalytically active metal indicates that the use of the same catalyst bed as both sorbent and catalytic reactor is feasible.

The baseline catalyst's sorption capacity varies greatly with the contaminant adsorbed. Similar concentrations of Freon-113 and thiophene, 0.49 and 0.43 mg/L respectively, adsorbed at over 100 mg/cc of catalyst; while 0.35 mg/L of bromotrifluoromethane was adsorbed at only 1.9 mg/cc of catalyst. Dichloromethane, at an influent concentration of 0.198 mg/L, was adsorbed by the catalyst at 13.7 mg/cc. The adsorption data for CARS indicates that there is an inverse relationship between a contaminants volatility and its adsorptivity.

Due to the catalyst's relatively low affinity for bromotrifluoromethane adsorption, two other sorbents were tested. An activated carbon fiber derived from the carbonization of kynol fibers (ACF-1605 distributed by American Kynol, Inc.) showed little capacity for bromotrifluoromethane adsorption. More promising results were obtained by using Carbosieve S-III (available through Supelco), a carbon based molecular sieve with a 15 to 40 angstrom internal pore matrix. This product was originally manufactured for the adsorption of low molecular weight hydrocarbons in chromatography gas streams, making it suitable for the adsorption of similarly sized halocarbons. The Carbosieve's capacity was established at 13.6 mg/cc with a stream concentration of 0.35 mg/L bromotrifluoromethane. Its capacity was 7.2 times greater than activated carbon's capacity. Previous work at UMPQUA has shown this Carbosieve to be thermally regenerable.<sup>5,6</sup> The addition of carbosieve to the sorption/catalyst bed will significantly increase the beds overall capacity when low molecular weight halocarbons are present in the contaminated air stream.

### **3.2 Desorptions**

The configuration of the final test stand depends on the temperature dependent desorption of contaminants from the catalyst's surface. If desorption occurs at temperatures below the catalytic hydrogenation temperature of 125 to 200 C, a single pass system will bleed an excessive amount of contaminants before they are reduced. Desorptions were performed on the activated carbon and baseline catalyst with loadings of Freon-113 and dichloromethane (Figures 2 and 3). The temperature was raised from 23 C to 125 C at 1 C/minute with a continuous flow of nitrogen gas through the bed. The effluent gas was analyzed by shots on a gas chromatograph. These data indicate that: both the activated carbon and the baseline catalyst desorbed significant concentrations of both contaminants before an effective catalytic temperature was reached, and that the catalyst desorbed higher concentrations of halocarbon sooner than the activated carbon. Since the contaminants

# Thermal Desorption of Freon-113

T=23 to 125 at 1 C/min, 21 cc/min Nitrogen

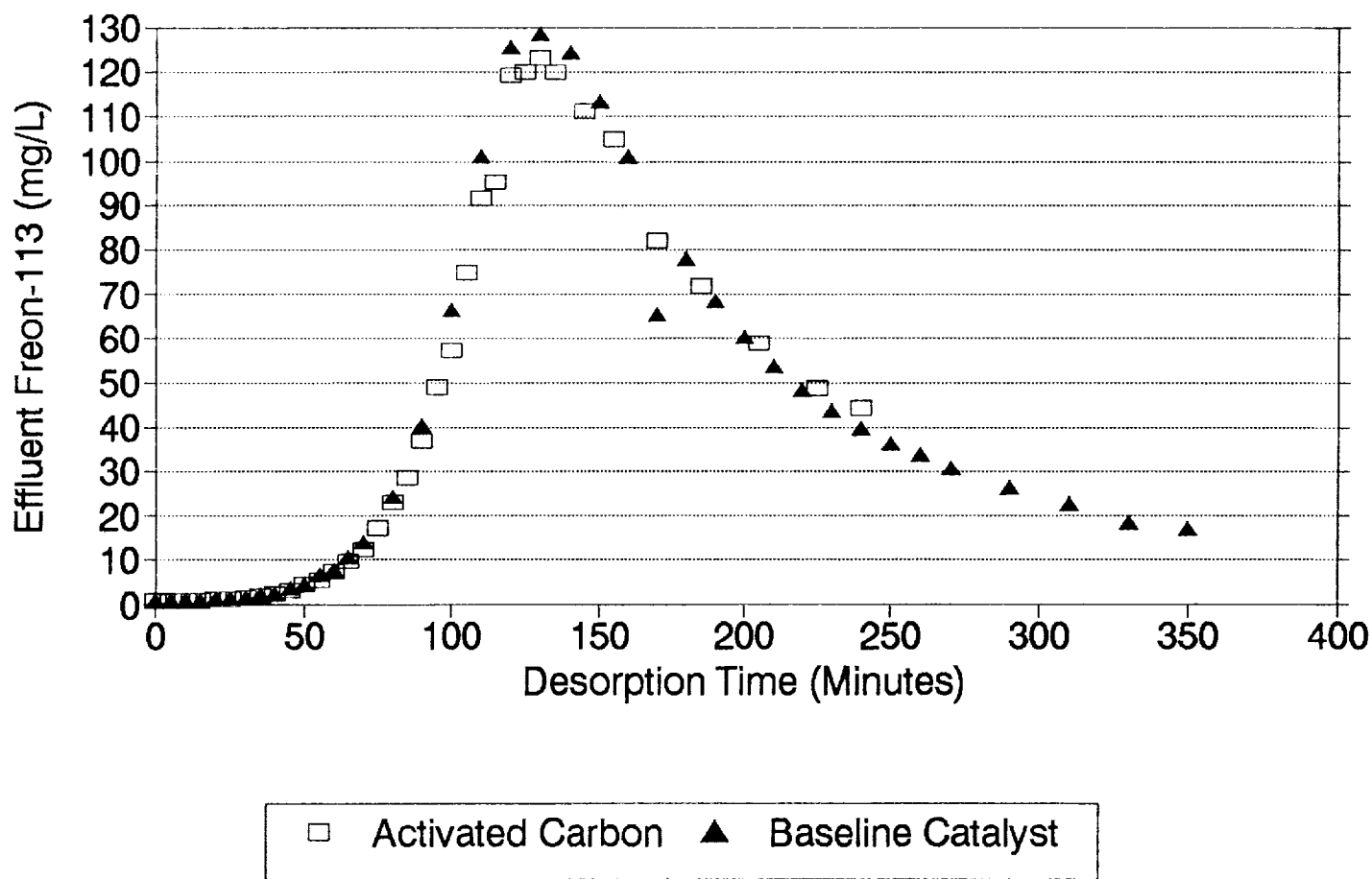


Figure 2. Thermal Desorption of Freon-113

# Thermal Desorption of Dichloromethane

T=23 to 125 at 1 C/min, 21 cc/min Nitrogen

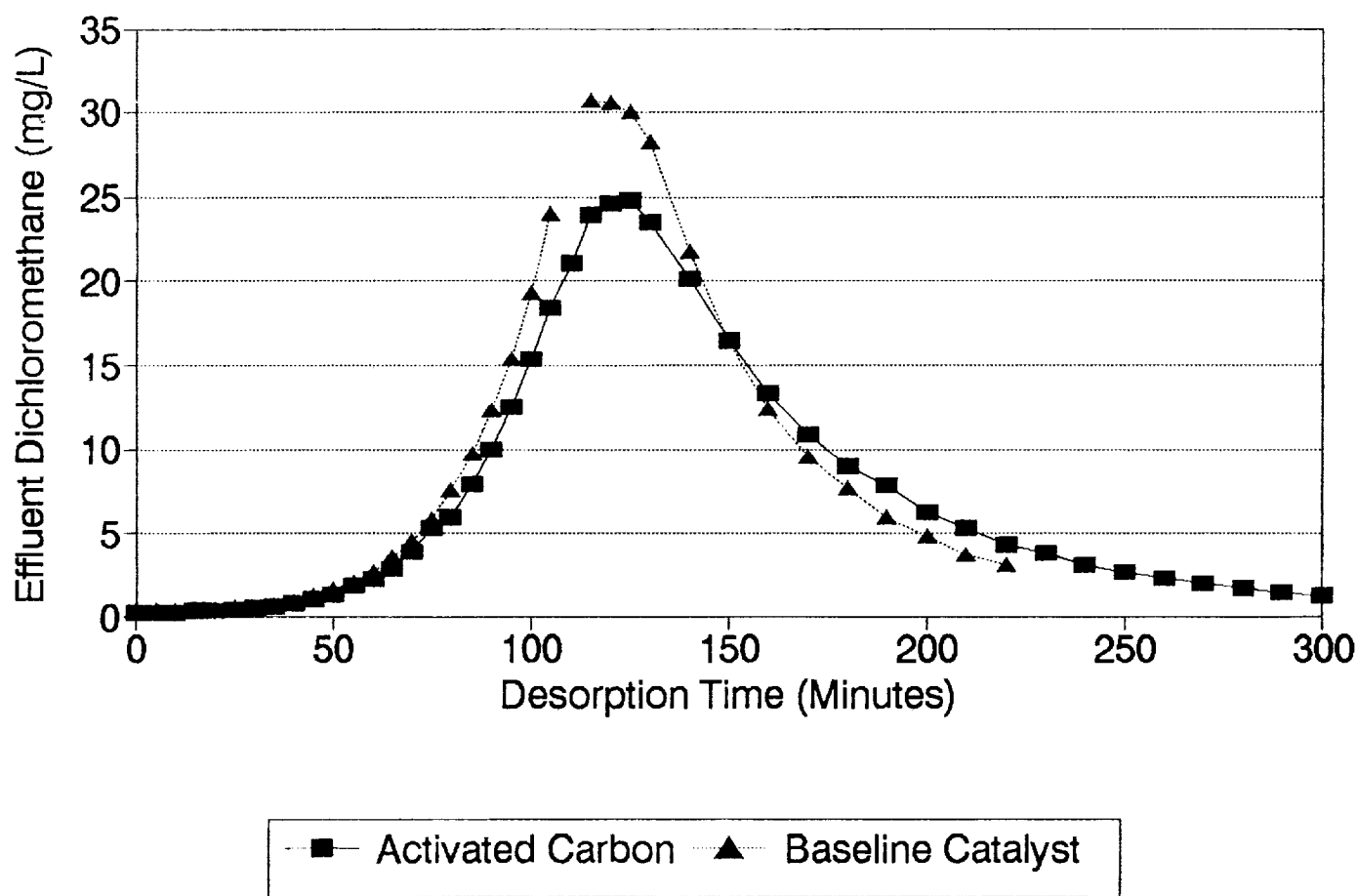


Figure 3. Thermal Desorption of Dichloromethane

desorb at a temperature below which the catalyst is effective, a single pass system in which hydrogen passes through a heated bed loaded with contaminants will bleed an unacceptable amount of contaminants into the hydrogen stream. This problem is compounded by the formation of partially hydrogenated intermediates more volatile than the original contaminants.

There are two possibilities to circumvent this problem. Given enough gas volume, the reactor can be pressurized with hydrogen and then heated until all halocarbons have been reduced. Depending on the amount of halocarbons adsorbed on the bed, this method might require high hydrogen pressures to supply sufficient reducing agent. This method allows halogen acids to remain in contact with the catalyst blocking catalytically active sites and requiring a long desorption time to clear the bed at the end of the regeneration cycle.

The second possibility involves recirculating hydrogen and partially reduced by-products through the reactor and a lithium hydroxide bed to adsorb the acid gases. The acid gases no longer compete for catalytic sites. Hydrogen consumed in the reactor can be replaced by maintaining the system at a constant pressure using hydrogen as the makeup gas. Recirculation is continued until all of the halocarbons are reduced. This is the process configuration chosen as the final system configuration for this project.

### **3.3 Multiple Contaminant Adsorption Study**

A 4cc bed of the baseline catalyst was challenged with a multiple contaminant stream to determine how the component's adsorption behavior interact. The contaminant air stream was assayed using the gas chromatograph and comparing the peak heights to those of standard concentrations prepared in the lab. The air stream contained:

- 0.51 mg/L bromotrifluoromethane
- 0.55 mg/L dichloromethane
- 0.54 mg/L Freon-113
- 0.47 mg/L thiophene
- 0.38 mg/L trichloroethylene

The bed was challenged at a flow rate of 1000 cc/minute for 1270 minutes (Figure 4).

The sorbent retained an insignificant amount of bromotrifluoromethane, and breakthrough occurred immediately. Dichloromethane, Freon-113, and thiophene exceeded their influent concentrations after their complete breakthrough occurred. By performing a manual integration of the adsorption curves, it was calculated that the sorbent initially retained 67 milligrams of dichloromethane but then released 46 milligrams before the end of the run, thereby retaining only 21 milligrams. The sorbent also initially retained 150 milligrams of Freon-113 but then released 83 milligrams, thereby retaining only 67 milligrams. Competition from more strongly adsorbed species such as thiophene and trichloroethylene displaces a

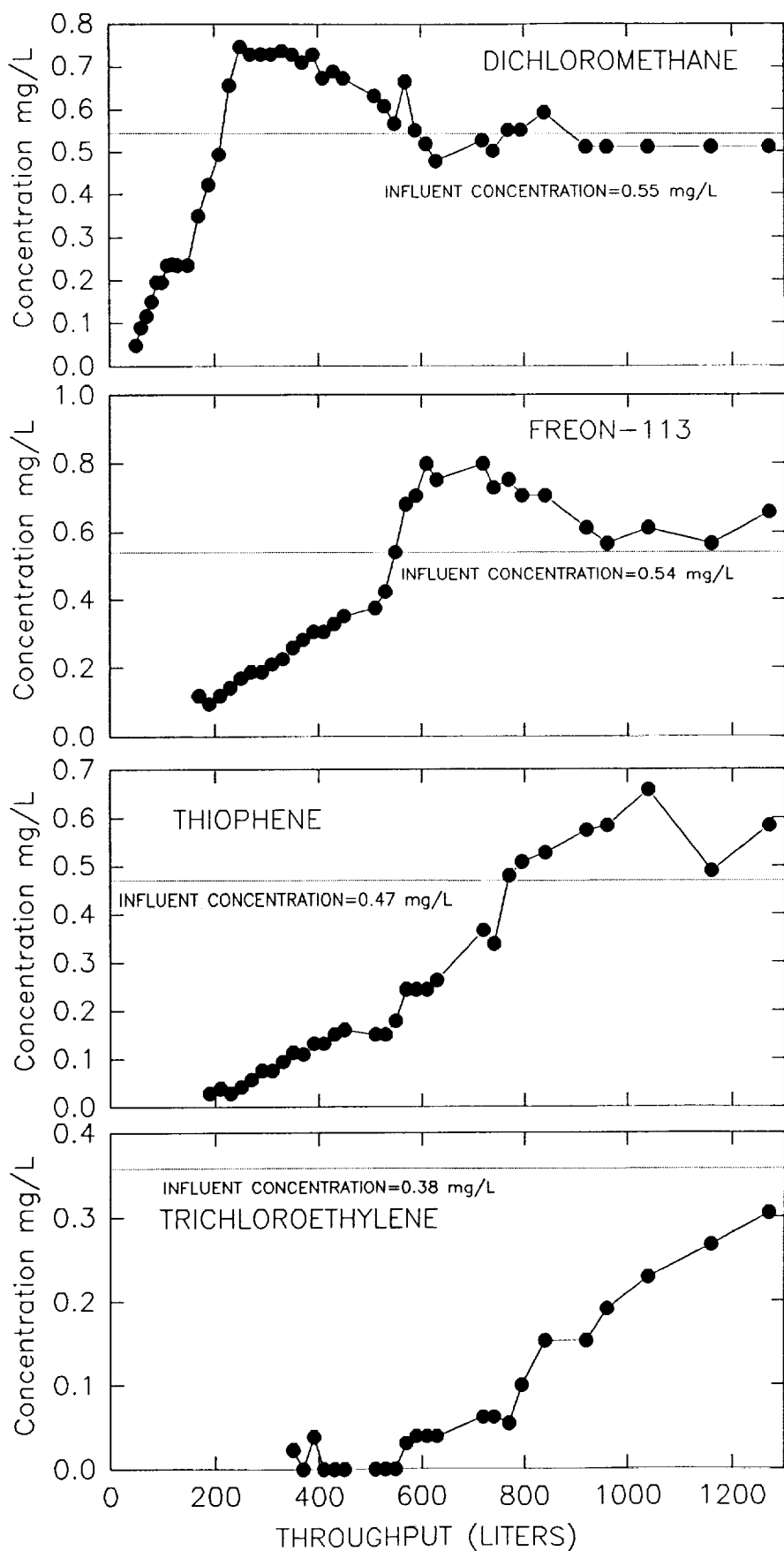


Figure 4. Multiple Contaminant Adsorption Study

portion of the less strongly adsorbed species. A sorbent bed exposed to a multiple contaminant stream will be limited in sorption time by the least retained, more easily displaced contaminant.

The more volatile contaminants such as bromotrifluoromethane and dichloromethane are not well retained by this type of activated carbon. The addition of Carbosieves which have a greater affinity for the more volatile organics will greatly extend the effective adsorption capacity of a sorbent bed.

#### **4.0 CATALYST ACTIVITY TESTING**

##### **4.1 Catalyst Test Apparatus**

Five catalysts were prepared and tested for halocarbon reduction. Not all catalysts were tested on all of the contaminants, but comparisons were made among pairs of catalysts to determine the varying activities of each. The apparatus used for catalyst testing, with the exception of bromotrifluoromethane which is a gas at room temperature, is illustrated in Figure 5.

A regulated flow of hydrogen is split with one stream passing through a gas bubbler to mix with the contaminant vapor. The contaminant/hydrogen stream is then diluted to the desired concentration with uncontaminated hydrogen from the second branch of the split stream. Early attempts to mathematically determine the halocarbon content by indicated flow rates of the contaminated and dilution stream proved untenable. Incomplete saturation of the contaminated stream and the lack of calibration tables for the flow tubes in relation to a mixed hydrogen/halocarbon stream combined with reading errors of the flow tubes and the effect of slight temperature changes on the halocarbon partial vapor pressure to produce large errors. It was decided that the influent concentration could be more accurately determined by use of a gas chromatograph and standards prepared by injecting a known quantity of halocarbon into a flask containing a known volume of air. When bromotrifluoromethane was used as the contaminant, its vapor was mixed directly with a hydrogen stream.

The mixed contaminant/hydrogen stream then passes through individual flow control valves for each reactor. A backpressure regulator maintains a constant pressure drop across the flow control valves for accurate control. The reactors are composed of 1/2 inch diameter stainless steel tubing with a 0.035 inch wall and porous metal frits as end plugs to contain the catalyst. A temperature controller using a low mass thermocouple to measure each reactor's external surface temperature controls a heating tape wrapped around the reactor to maintain



# CARS Catalyst Test Apparatus

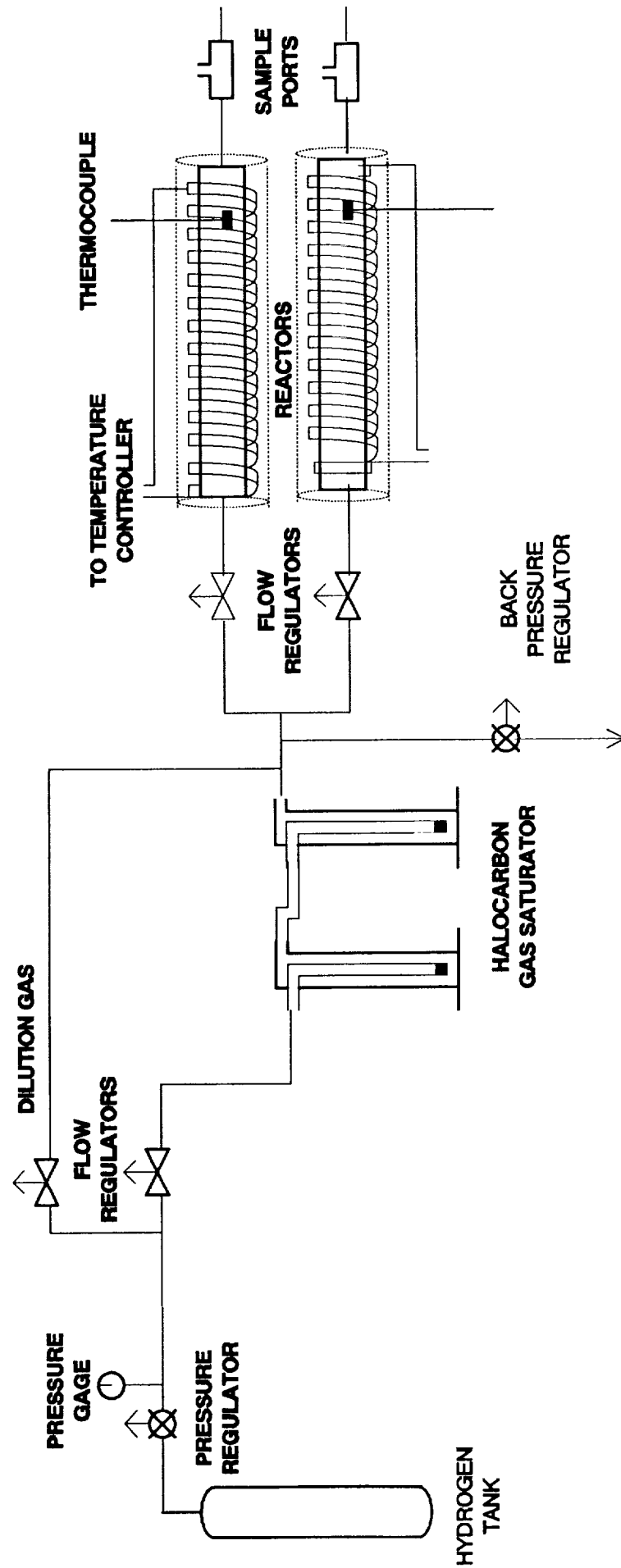


Figure 5. Catalyst Test Apparatus

the reactors' temperatures. Insulation is placed around each reactor to minimize heat loss and reduce the temperature gradients across the reactors.

Early in the catalyst testing, the method of effluent gas analysis was changed. Originally, the effluent gases were to be bubbled through a sodium hydroxide solution and analyzed for pH changes and halogen content to determine the catalysts' effectiveness at halocarbon reduction. This method would not have indicated the types or quantities of intermediate products. The effluent gases were instead analyzed using a gas chromatograph. Information regarding the presence of unreacted halocarbons, partially hydrogenated intermediates and the final products, alkanes, is more informative when comparing catalysts. The large number of possible intermediate by-products precludes the identification and quantization of all peaks observed from the gas chromatograph. Catalyst comparisons were based upon the production of alkanes and comparative heights of the other peaks.

#### 4.2 Hydrogen Reduction Reactions

The reduction of most halogenated and sulfonated organic compounds is a series of many individual reductions. For each halogen or sulfur to carbon bond, one hydrogen reduction must occur. Dichloromethane, for example, requires two separate reductions producing methane and two hydrogen chlorides:



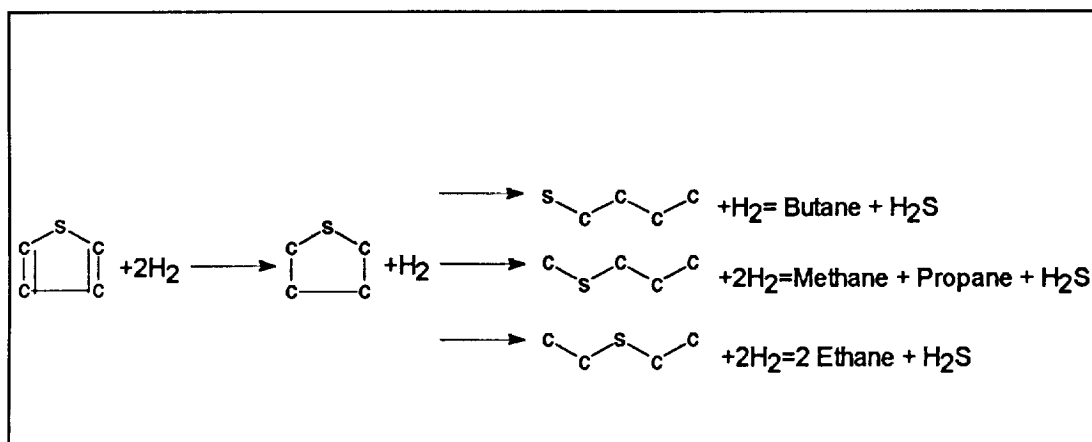
Results of catalyst runs in which dichloromethane was reduced show that chloromethane is present in the effluent gas.

The hydrogenation process becomes more complicated when reducing Freon-113. The complete reduction of Freon-113 to ethane requires six separate reductions. Each chlorine and fluorine is individually removed, resulting in over thirty possible intermediate by-products. Results of catalyst runs have also shown that the carbon-carbon bond in Freon-113 is susceptible to hydrogen reduction. Both methane and chloromethane have been detected in its effluent gases.

Carbon-carbon double bonds are more susceptible to hydrogenation than carbon-halogen bonds. When a bed of the baseline catalyst at room temperature was loaded with trichloroethylene and purged with nitrogen and then purged with hydrogen, a cloud of hydrogen chloride gas was expelled by the reactor. The reactor was warm to the touch afterwards. The energy released by the hydrogenation of the double bonds also causes the carbon-chlorine bonds to react. Trichloroethylene, when reduced at 125 degrees C, shows methane in the effluent, indicating reduction of the carbon-carbon bond.

Most of the intermediate reduction by-products of thiophene have not been identified.

It has been observed that methane, ethane, propane, and butane are all present in the effluent when thiophene is catalytically reduced. Butane is the most abundant by-product, indicating that the thiophene ring structure is most often cleaved at the sulfur-carbon bond producing thiobutane. Thiobutane will reduce to butane and hydrogen sulfide. The presence of the other alkanes implies that the carbon-carbon bonds in the ring structure are sometimes cleaved. This may occur when the double bonds in the ring structure are reduced. The heat of this reduction, compounded with the ring stresses, may produce a reduction between two carbons producing methyl propyl sulfide or diethyl sulfide. The subsequent desulfonating of these compounds would lead to methane, ethane, and propane production, as shown in Figure 6.



**Figure 6. Thiophene Reduction Reaction Steps**

### 4.3 Results of Catalyst Comparisons

Five different catalysts were prepared for this project using an activated carbon support. The same type of carbon substrate and parameters for thermal processing were used for all of the catalysts. The amount of metal loading is by percent of the original substrates mass. The catalysts tested were:

- 5% Ruthenium, 20% Platinum (The baseline catalyst)
- 5% Ruthenium, 20% Platinum, 10% Molybdenum
- 5% Nickel
- 5% Ruthenium, 5% Platinum
- 5% Palladium, 5% Platinum

These catalysts all showed varying but significant activity toward halocarbon reduction. Results will be discussed in a series of comparisons between catalysts under similar conditions of temperature, contaminant concentration, and reactor residence time.

#### **4.3.1 5% Nickel v.s. Baseline Catalyst for Freon-113**

The 5% nickel catalyst and the baseline catalyst were run under similar conditions to determine their relative abilities to reduce Freon-113. The runs were performed at 200 degrees C and a reactor residence time of approximately 2 minutes with influent Freon-113 concentrations of 14.1 and 22 mg/L. The results of the effluent gas analysis are presented on a bar graph in Figure 7. The retention times of the various by-products separated in a gas chromatograph column are graphed against their peak heights. The identities of these by-products and their actual concentrations were not established but are not necessary for a specific comparison between the two catalysts. Generally, the larger, less hydrogenated by-products will have a longer retention time. It should also be noted that a longer retention time means that the gas chromatograph peak will be broader and represent a greater concentration for the same peak height.

Under the previously mentioned reaction conditions, the nickel catalyst produced only 50% of the ethane (RT=35 seconds) and 36% of the methane (RT=19 seconds) that the baseline catalyst produced. The nickel catalyst allowed more partially reduced by-products to pass, indicating its lesser activity. Although a nickel catalyst could be effective where a longer residence time/larger bed size would be feasible, the aerospace priorities of low mass and energy efficiency makes this catalyst less attractive. No further catalytic runs were performed on the nickel catalyst.

#### **4.3.2 5%Ru, 5%Pt v.s. 5%Pd, 5%Pt**

Catalysts composed of 5%Ru, 5%Pt and 5%Pd, 5%Pt were challenged with a series of three contaminants: Freon-113, dichloromethane, and then bromotrifluoromethane. These catalysts were tested simultaneously and received the same concentrations of contaminants.

The catalysts were challenged with Freon-113 at 125 degrees C (Figure 8) and then 200 degrees C (Figure 9). As in the previous comparison, the effluent gas is analyzed with a gas chromatograph and the peak heights are graphed against their retention times (RT). As expected, both catalysts showed greater activity at the higher temperature, even when considering the increase in residence time. At both temperatures, the ruthenium catalyst outperformed the palladium catalyst as indicated by its production of more methane and ethane. The ruthenium catalyst increased its ethane production by a factor of nine due to the rise in temperature, while the palladium catalyst increased its ethane production by a factor of four. At 125 C, the palladium catalyst allowed less of the larger partially hydrogenated products through (RT>70).

The palladium catalyst showed more promise when the columns were challenged with

# Catalyst Comparison

## Freon-113 at 200 deg C

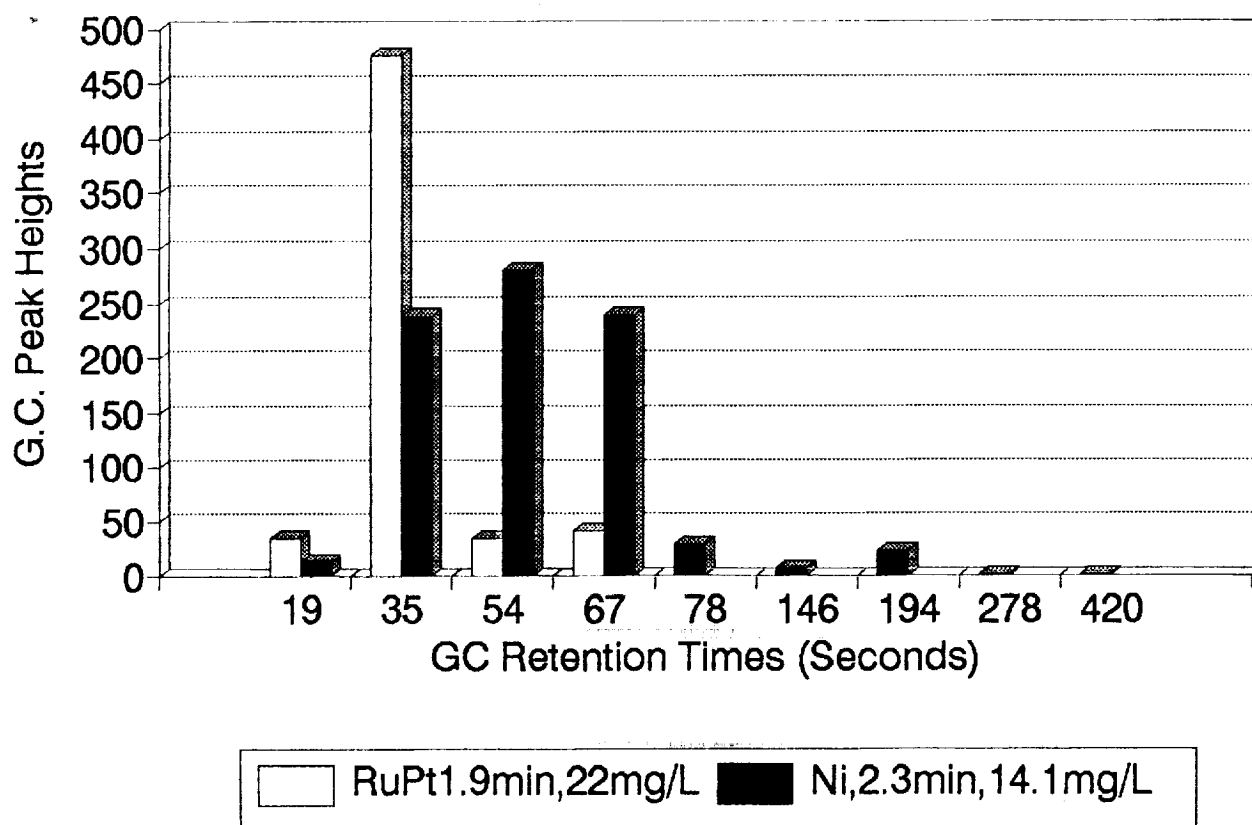


Figure 7. Baseline Catalyst vs. 5% Nickel Catalyst for the Reduction of Freon-113 at 200 Degrees C

# Catalyst Comparison

125 C, 31.2mg/L Freon-113

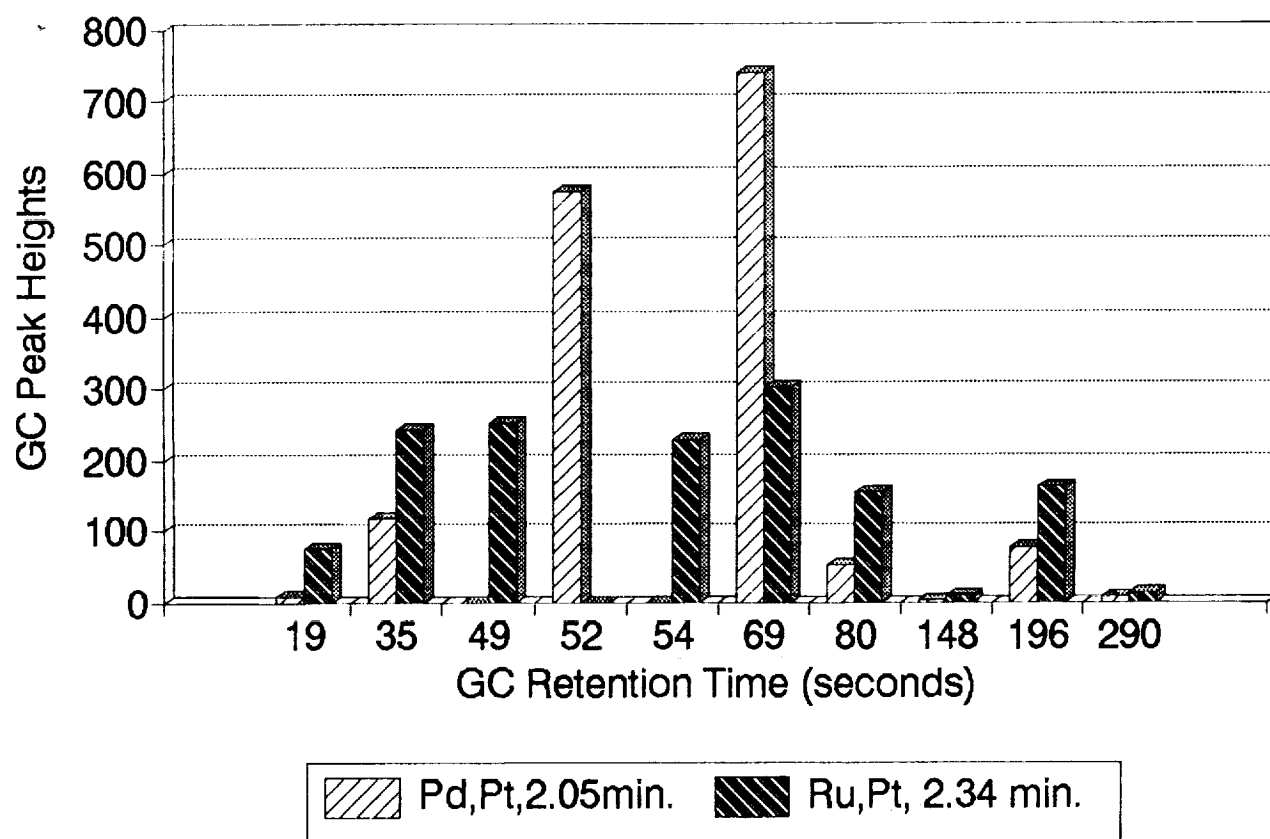


Figure 8. 5%Pd, 5%Pt v.s. 5%Ru, 5%Pt Catalyst for the Reduction of Freon-113 at 125 Degrees C

# Catalyst Comparison

200 C, 35.6 mg/L Freon-113

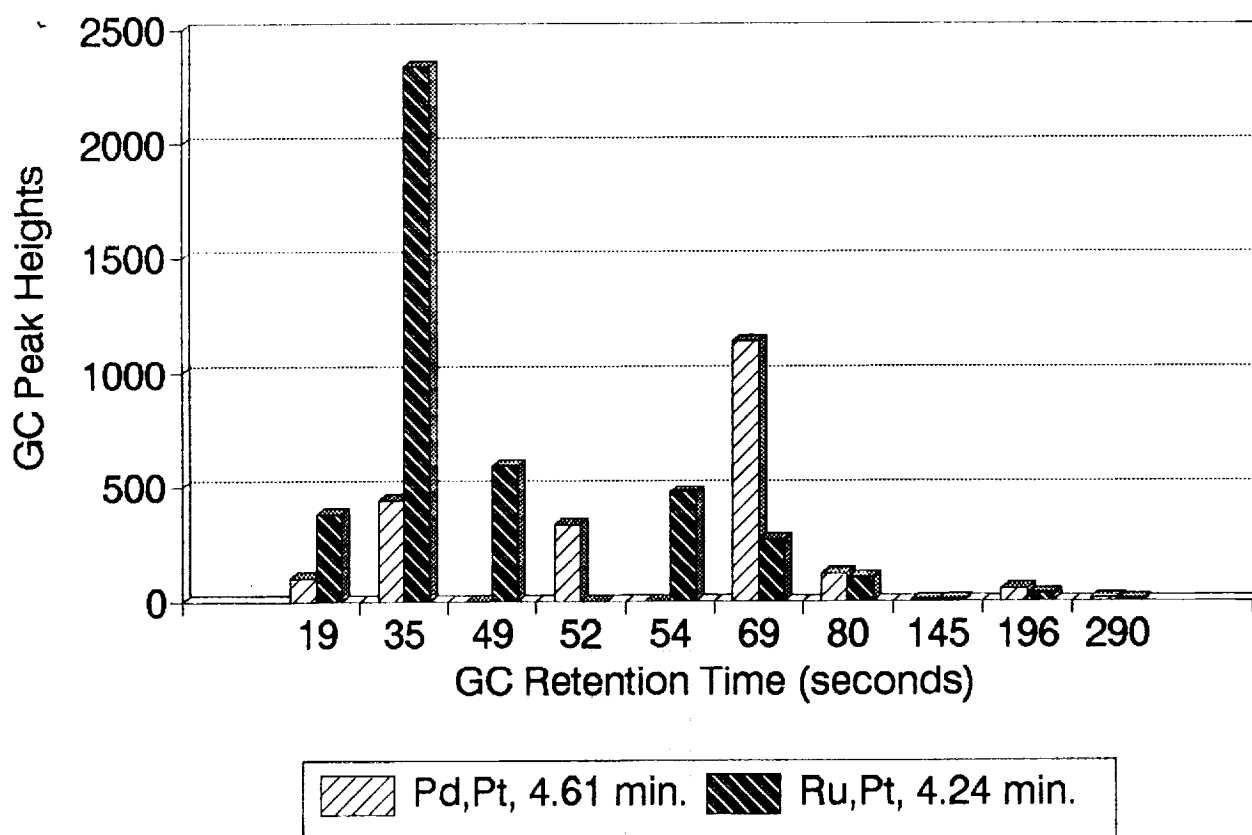


Figure 9. 5%Pd, 5%Pt, v.s. 5%Ru, 5%Pt Catalyst for the Reduction of Freon-113 at 200 Degrees C

12 to 16 mg/L of dichloromethane for two weeks. Both reactors were at 125 C with contact times of 1.8 to 2.4 minutes. The palladium catalyst allowed only half as much unreacted dichloromethane through: 3 mg/L as compared to 6.3 mg/L for the ruthenium catalyst. The palladium catalyst had almost three times the amount of intermediate product, chloromethane, in its effluent but did produce slightly more methane.

Neither of these catalysts was able to match the effectiveness of the baseline catalyst for dichloromethane reduction. When challenged with 49 mg/L of dichloromethane at a contact time of 1.50 minutes and a temperature of 125 C, it allowed only 4.35 mg/L breakthrough of dichloromethane. The extra 15% platinum content of the baseline catalyst is the only difference between it and the 5%Ru, 5%Pt catalyst, and therefore is the reason for the baseline catalyst's greater activity.

The catalysts were then challenged with 7.6 mg/L of bromotrifluoromethane at 125 C and then 200 C. At 125 C, a reactor residence time of 6 minutes was established and the effluent gas tested for methane and other by-products. The ruthenium catalyst produced three times the amount of methane, indicating a greater activity. The ruthenium catalyst did allow a significant amount of breakthrough, 6 mg/L of bromotrifluoromethane but the palladium catalyst allowed 6.3 mg/L breakthrough. This greater performance was repeated at 200 C where the ruthenium catalyst produced twice as much methane.

Overall, both catalysts produced results indicating the ability to reduce these three halocarbons to alkanes. Although the palladium catalyst showed a greater activity toward dichloromethane reduction, the ruthenium catalyst was more effective against Freon-113, the major component in the TCCS model. This makes the ruthenium catalyst more useful for our current purposes. The additional platinum in the baseline catalyst increases the activity toward dichloromethane reduction.

#### **4.3.3 The Addition of 10% Molybdenum to the Baseline Catalyst**

The addition of molybdenum to the baseline catalyst was an attempt to enhance its ability to react with sulfur containing compounds. Molybdenum by itself or in combination with nickel or cobalt has demonstrated superior performance for the hydrodesulfurization of sulfur containing organic compounds. Since the system was already set up with the bromotrifluoromethane influent system and the baseline catalyst had not been tested with this influent, the baseline catalyst and the baseline catalyst plus 10% molybdenum were first challenged with this contaminant. Figures 10 and 11 track the reactors' influent concentrations, residence times, and effluent gas components compared to the total amount



# 5%Ru,20%Pt on Carbon

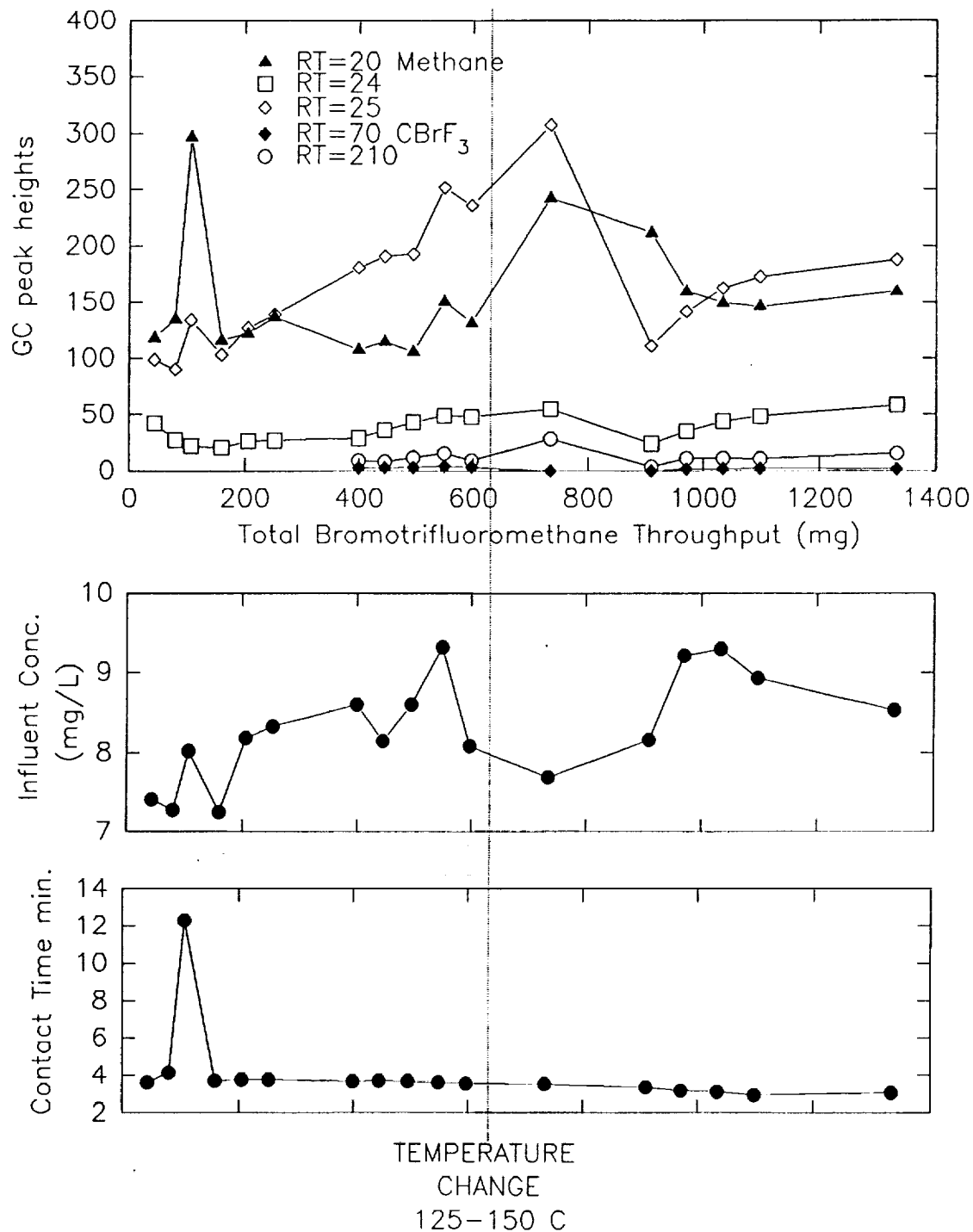


Figure 10. Baseline Catalyst Reduction of Bromotrifluoromethane

# 5%Ru,20%Pt,10%Mo/Carbon

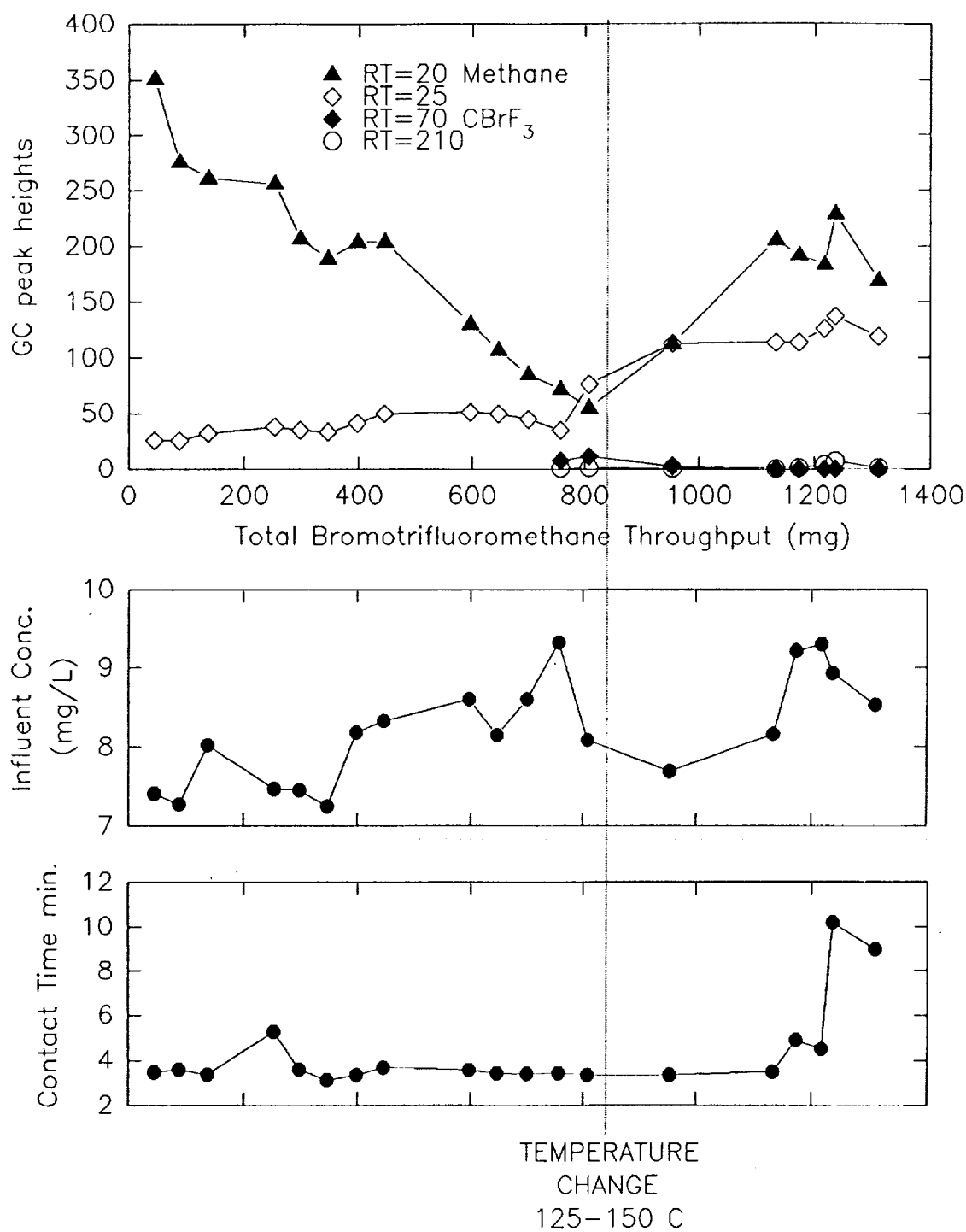


Figure 11. Baseline/Molybdenum Catalyst Reduction of Bromotrifluoromethane

of bromotrifluoromethane throughput. The data was accumulated over a span of forty days and included a change in temperature from 125 C to 150 C.

The molybdenum containing catalyst initially produced more methane than the baseline catalyst, but its production decreased rapidly without a corresponding increase in the production of other by-products. When comparing the total amounts of effluent by-products from the two reactors, one notices that the molybdenum catalyst's effluent is lacking carbon mass. The two reactors were fed the same contaminant concentrations, but the molybdenum containing catalyst produced less of all of the by-products. This is only possible if the molybdenum catalyst is producing and retaining tars or reducing the contaminants to elemental carbon.

The catalysts were cleansed of by-products by a flow of hydrogen at operating temperature. When an analysis of the effluent gas showed that no more by-products were being desorbed by the catalysts, the reactors were cooled and the catalysts removed and weighed. The molybdenum catalyst had gained 0.2 grams while the baseline catalyst had lost a slight amount of weight, most likely due to the loss of ambient moisture previously adsorbed before being placed in the reactor. Since the molybdenum catalyst did not produce any larger compounds indicative of intermediates in tar production, it had most likely produced carbon. This coking had not affected the catalyst's activity during this run; however, it might over a longer span of time.

## **5.0 THE FINAL TEST STAND CONFIGURATION AND RESULTS**

### **5.1 The Final Test Apparatus**

The final test system (Figure 1) is operated in two separate cycles: adsorption and catalytic regeneration. In the first cycle, a contaminated air stream flows through the carbon/catalyst bed where the contaminants are transferred from the air to the sorbent surface. The effluent from the sorption bed is continuously monitored for organic contaminants by a hydrocarbon analyzer which uses a flame ionization detector and will detect a breakthrough of less than 0.01 mg/L of the components in the contaminant stream.

The sorbent bed is composed of 4cc of the baseline catalyst and 4cc of Carbosieve S-III mixed together. The Carbosieve shows a much greater affinity for the smaller organics such as bromotrifluoromethane. The incorporation of Carbosieve in the bed dramatically increases the systems sorption capacity for the mixed contaminant load.

The second cycle is the catalytic reduction/sorbent regeneration cycle. During regeneration the flow path is switched to include the CARS bed, a hydrogen source, a pump

for gas recirculation, and a lithium hydroxide bed for acid gas removal. The system is first purged with nitrogen to remove excess oxygen, which would react with hydrogen. The system is then purged with hydrogen and pressurized to approximately 14 PSIG. Hydrogen is kept on line to supply makeup hydrogen as it is used up in the reaction. The reactor is then heated at a rate of 5 C/minute until operating temperature is reached.

As hydrogen is recirculated through the reactor, intermediate by-products and nonreacted contaminants desorb into the hydrogen gas along with the acid gases and alkanes produced by hydrogen reduction. The acid gases are removed when they react with the lithium hydroxide bed to form nonvolatile lithium halides and water. The hydrogen sulfide produced by thiophene reduction will form lithium sulfide, which is also nonvolatile. The partially reduced organics, unreacted hydrogen, and alkane products are recirculated through the catalytic reactor until an acceptably small amount of non-reduced organics are left in the hydrogen stream. For the purposes of this project, the gases are then purged from the reactor with a flow of nitrogen at operating temperature. The reactor is then cooled to prepare for the next adsorption cycle.

In the TCCS model, Freon-113 is the major halogenated constituent, and this is reflected in the model contaminant mixture chosen to test the recirculation reduction system. The other components were added at the minimum measurable concentrations. In later runs, the detection limit for bromotrifluoromethane was reduced, allowing for lower influent concentrations more in proportion with its concentration in the TCCS model.

## 5.2 The First Run

The first contaminant stream tested was composed of:

Bromotrifluoromethane	0.50 mg/L
Dichloromethane	0.078 mg/L
Freon-113	0.96 mg/L
Thiophene	0.086 mg/L
Trichloroethylene	0.092 mg/L

The adsorption was continued for 200 minutes at a flow rate of 500 cc/min. for a throughput of 100 liters. The only contaminant to break through was bromotrifluoromethane, which started breaking through at 80 minutes and reached a concentration of 0.1 mg/L by the end of the 200 minutes.

The catalytic reduction/regeneration cycle for this adsorption was not maintained at any one temperature or hydrogen pressure. Parameters were varied to determine the effects on the system. As the reactor bed was initially heated up, a variety of partially hydrogenated contaminant by-products were detected in the recirculating hydrogen. None of the original

contaminants were detected in the effluent, indicating that the contaminants were reduced at least once before escaping the bed. The by-products of the initial reduction are either readsorbed and reduced again or continue to recirculate. It was also noted that a removal of some of the recirculating gas through the sample port caused a predictable reduction in the contaminants' concentration due to dilution by makeup hydrogen. The larger, less volatile by-products recovered partially from this reduction in concentration, whereas the more volatile components did not. The reactor's carbon retains a portion of these larger contaminants and re-equilibrates with the hydrogen gas when a sample is removed.

With over thirty possible intermediate by-products for Freon-113 alone, there are difficulties in quantitatively describing the progression of a catalytic regeneration run. The gas chromatograph has revealed fifteen major by-products whose peak heights have been recorded throughout these regeneration runs. Methane, ethane, propane, and butane have been identified by retention time. The catalytic reduction would be considered complete when these are the only peaks remaining.

A desorption of the remaining by-products was performed at 200 degrees C and a nitrogen flow rate of 10 cc/minute. It was found that some of the larger by-products were still being desorbed 1200 minutes later. A higher desorption temperature will reduce the required desorption time.

### **5.3 The Second Run**

The next adsorption run was performed at the same flow rate and duration as the first, using the same influent. At the end of the run, a breakthrough of bromotrifluoromethane at a concentration of 0.25 mg/L was detected. The previous desorption of contaminants was incomplete, and these retained contaminants competed with the influent for adsorption sites.

During the regeneration cycle, the reactor was maintained at 200 degrees C for the first 460 minutes and then at 250 degrees C for the rest of the run. Figures 12, 13, and 14 track the concentrations of fifteen of the by-products through the entire catalytic regeneration. The regeneration continued for approximately eight hours at a time; the dotted vertical lines on the graphs indicate the beginning of a day's run. Each night the system was cooled down to room temperature and the makeup hydrogen was turned off. There is a noticeable drop in the by-products' concentrations after each shutdown with the more volatile components being the most affected. Small gas leaks in the system cause a loss of some non-adsorbed contaminants.

There are trends in the contaminant concentrations relevant to all of the catalytic regenerations. When hydrogen is initially recirculated through the system at room

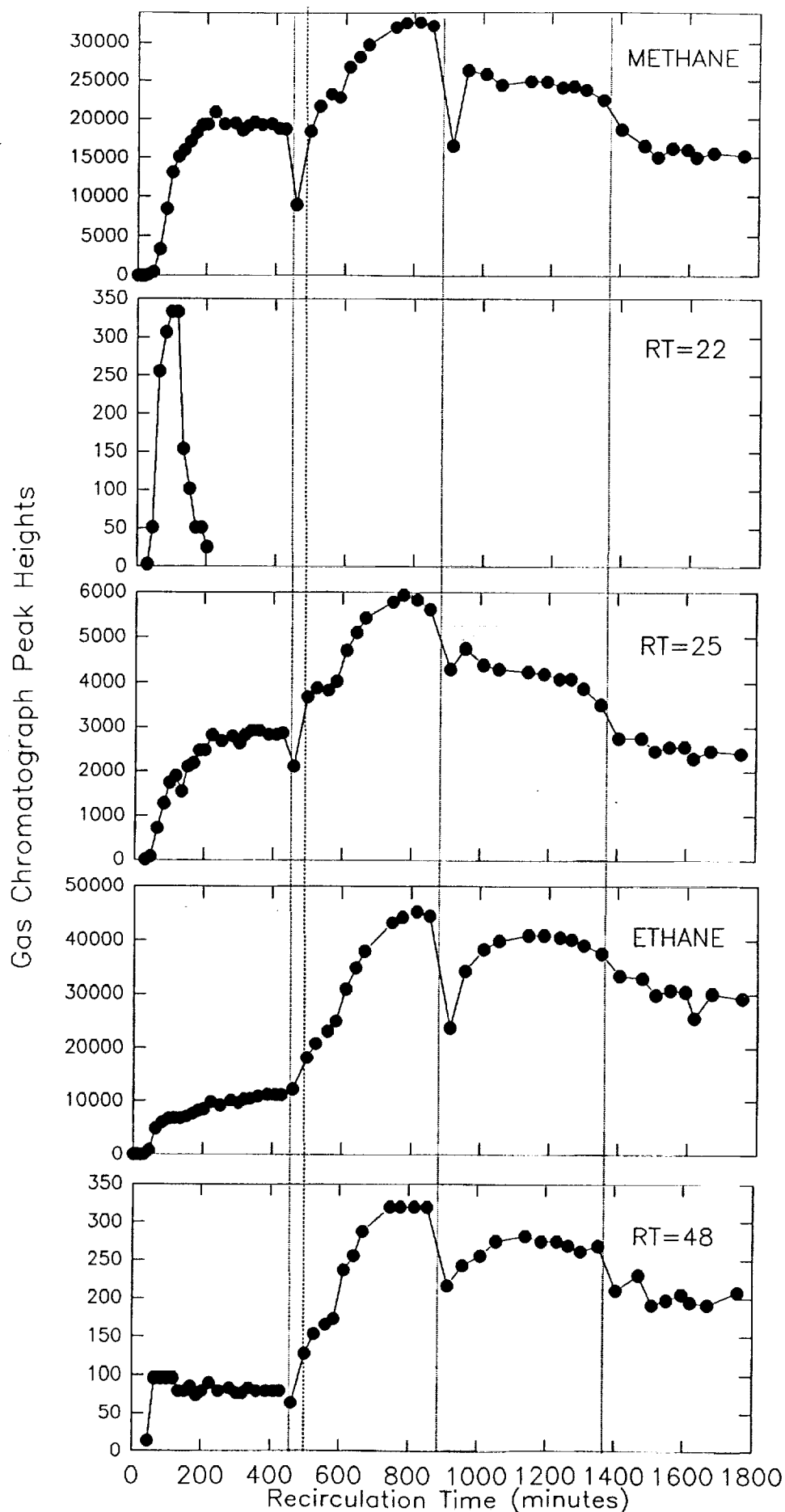


Figure 12. Final Test Stand's Second Regeneration Run

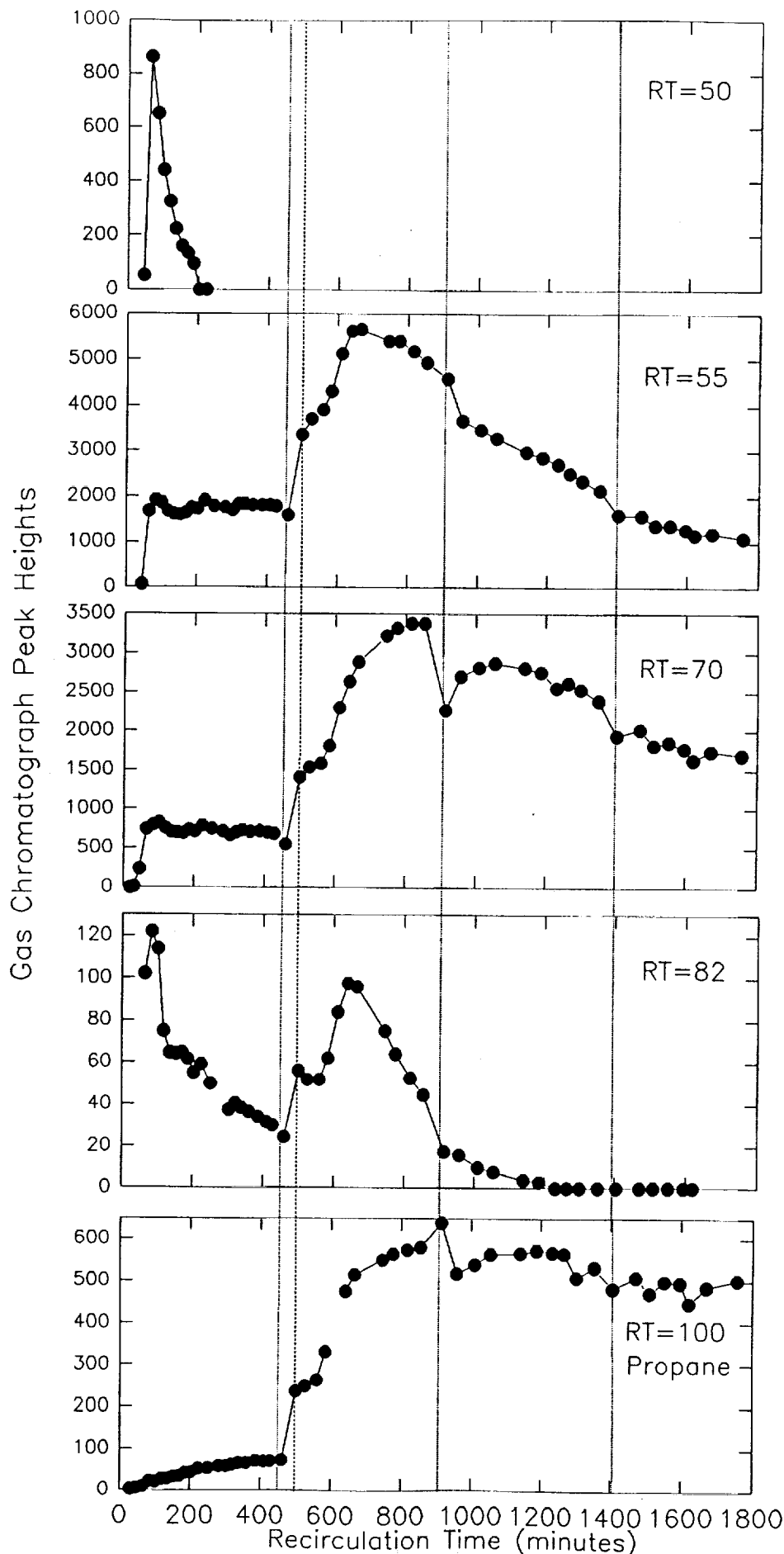


Figure 13. Final Test Stand's Second Regeneration Run

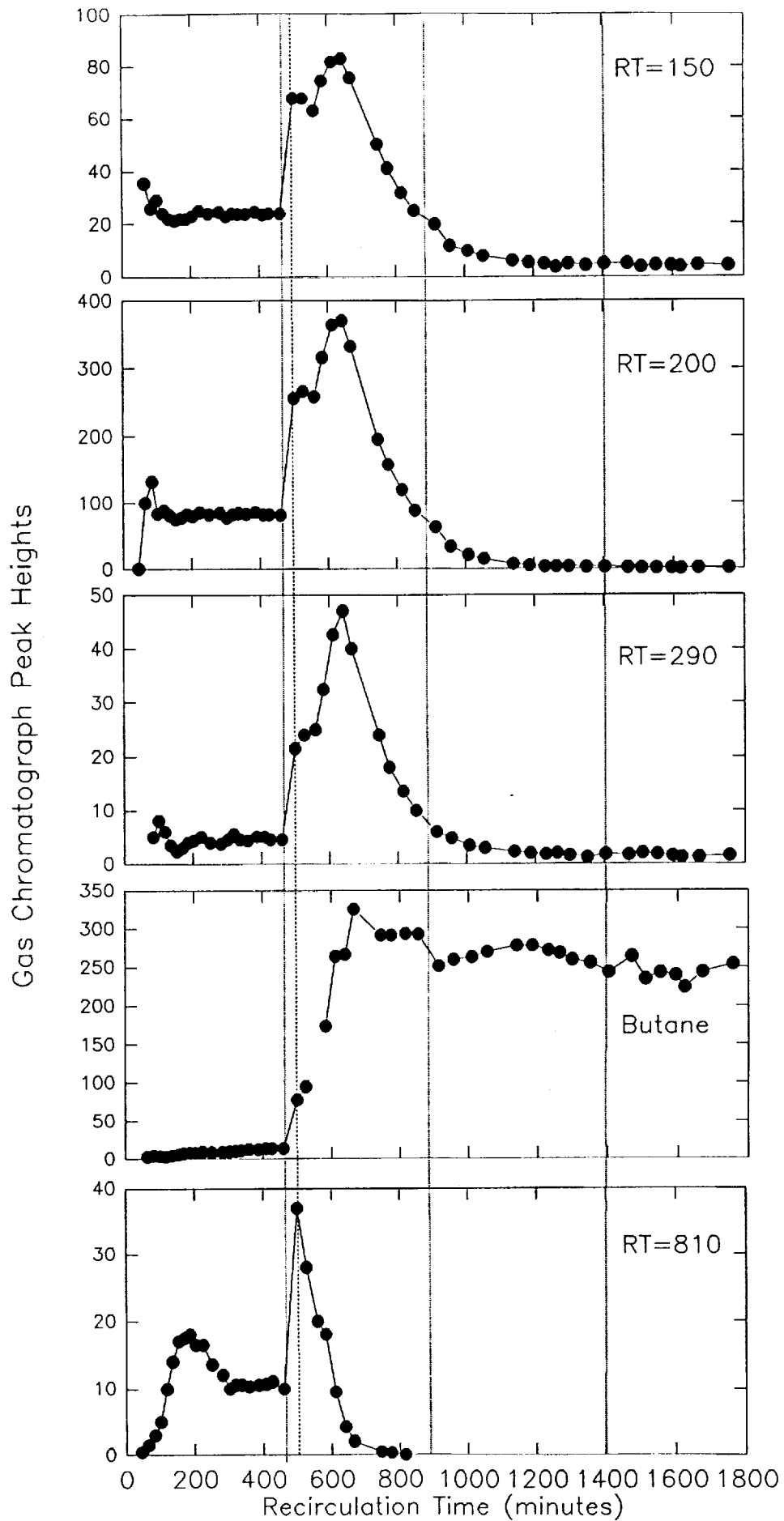


Figure 14. Final Test Stand's Second Regeneration Run



temperature, the only detectable compounds are a trace of methane and sometimes ethane. As the system is heated at a rate of 5C/minute, all detectable compounds start desorbing from the carbon surface and increase in concentration in the hydrogen gas. The more volatile by-products of hydrogenation increase in concentration in the gas stream faster since they are not well retained in the carbon bed. Some intermediate by-products, RT=22 and RT=50, are quickly reduced to alkanes; while others such as RT=810 require more time to be reduced. During about the first half of the run, intermediate products like RT=25, RT=48, RT=55, and RT=70 are being produced by the hydrogenation of larger by-products and are also undergoing reduction.

The peak at RT=810 is a by-product of thiophene reduction. It is most likely thiobutane, the sole source for the butane and propane by-products. This conclusion is supported by the fact that the production of propane and butane stops when RT=810 is depleted.

When the reactor temperature was raised from 200 to 250 C, indicated by the vertical dashed line, the concentration of all by-products in the hydrogen stream increased due to desorption from the carbon catalyst. There is also a noticeable increase in the rate of contaminant reduction. An increase in reactor temperature increases the amount of thermal energy available to activate the hydrogenation reactions. The higher temperature also increases the mobility of adsorbed species on the carbon surface and in the gas phase, and decreases the concentration of adsorbed species. The kinetics are most probably dominated by the thermal energy term.

#### 5.4 The Third and Fourth Runs

The third and fourth runs were both performed with a new contaminant stream consisting of:

Bromotrifluoromethane	0.068 mg/L
Dichloromethane	0.083 mg/L
Freon-113	1.67 mg/L
Thiophene	0.075 mg/L
Trichloroethylene	0.081 mg/L

This contaminant stream more closely reflects the ratios of contaminants in the TCCS model. Both of these adsorptions were performed at a rate of 500cc/minute for 200 minutes. Negligible breakthrough was detected in both runs.

The catalytic regeneration for the third run is shown in figures 15, 16, and 17. The regeneration temperature was ramped from 23 to 250 C at 5C/minute. Since this regeneration run was ramped to a higher temperature, the reducible components disappear more rapidly.

Gas Chromatograph Peak Heights

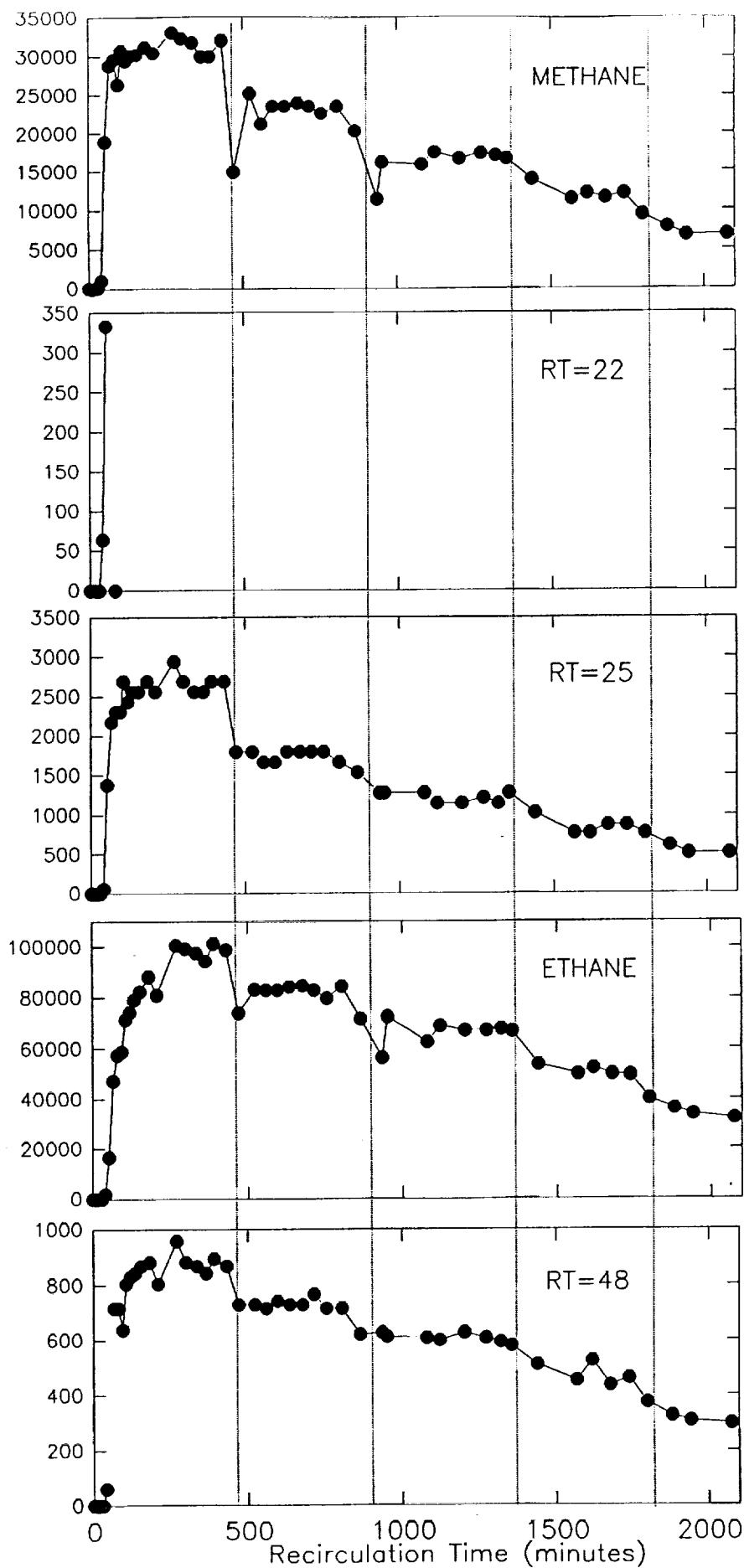


Figure 15. Final Test Stand's Third Regeneration Run

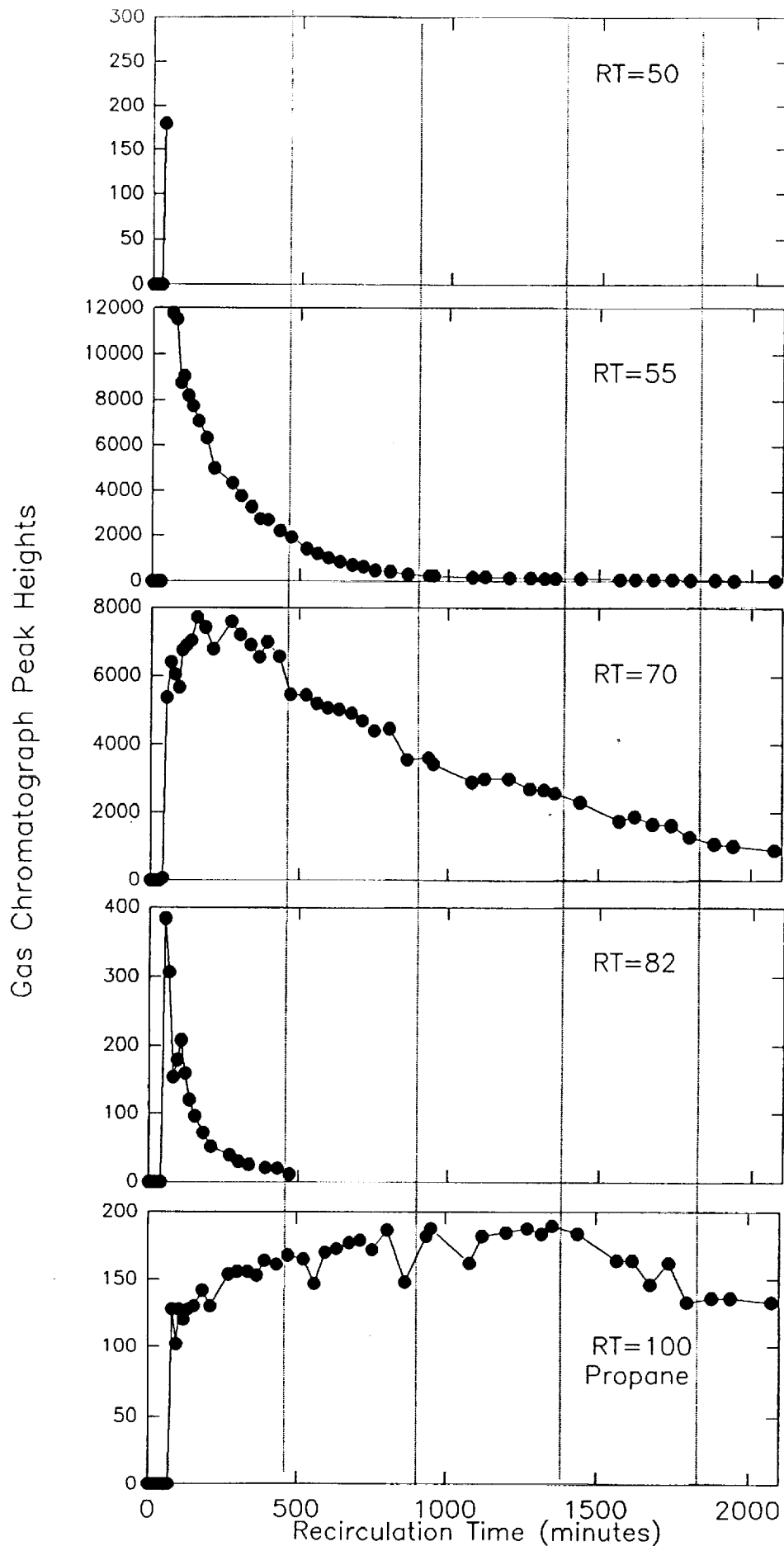


Figure 16. Final Test Stand's Third Regeneration Run

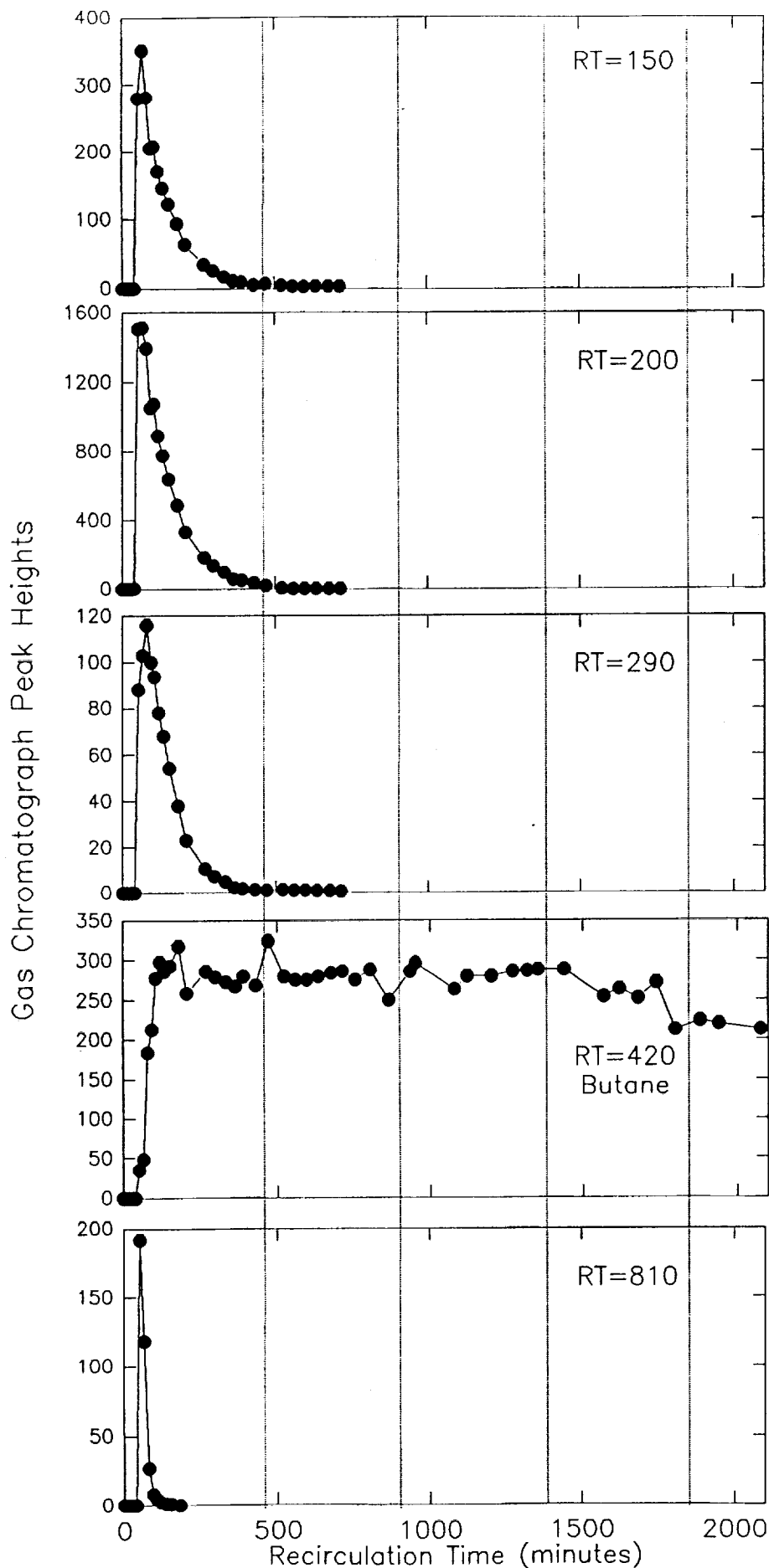


Figure 17. Final Test Stand's Third Regeneration Run

Some contaminants are very resistant to hydrogen reduction as exemplified by peaks RT=25, RT=48, and RT=70. Even after 2000 minutes, they still remain at significant concentrations in the gas stream. One possible delay is the poor exposure of contaminants to the catalyst. In an attempt to rectify this problem, the hydrogen reservoir was reduced in size for the fourth run. This reduced the gas volume outside the reactor from 59 cc to 18 cc. The results of the fourth regeneration are shown on figures 18, 19, and 20.

A comparison of the first 2000 minutes of the two runs indicates that no significant improvement in halogen reduction rate occurred due to the removal of the hydrogen reservoir. At 1937 minutes into the fourth run, the temperature was raised to 300 C to increase the rate of hydrogenation. All of the compounds present in the recirculation loop increased in concentration due to thermal desorption. The contaminants at RT=48 and RT=70 were reduced at a faster rate due to the 50 degree temperature increase. The by-product at RT=25 effectively mimics the methane concentration. Its concentration only decreases in between run times when leakage occurs. Its total inability to be reduced when the regeneration system is operating implies that it is probably a cyclic alkane or an inorganic by-product.

#### **5.5 The Fifth Run: The Molybdenum Catalyst**

The fifth run was performed using a mixed bed composed of 4 cc of the 5%Ru, 20%Pt, 10%Mo catalyst and 3.8 cc of Carbosieve recovered from the previous sorbent bed. The molybdenum containing catalyst was previously shown to be more active than the baseline catalyst in reducing bromotrifluoromethane. The same contaminant mixture and adsorption procedure used in runs 3 and 4 were used for this run. A little more breakthrough occurred in this adsorption run, but the amount was less than 0.01 mg/L. The extra breakthrough was probably due to the lower amount of Carbosieve in the sorbent bed.

The reactor temperature was ramped from 23 to 250 C at 5C/min for the first day of this regeneration (Figures 21, 22, and 23). After reaching temperature, none of the original challenge contaminants was identifiable in the recirculation gas mixture demonstrating that the first hydrogenation step occurs very rapidly. All of the compounds previously shown to be prone to hydrogen reduction were reduced significantly faster. The peak at RT=25 still showed no reduction. The peak at RT=290 appears to be the result of two different compounds with the same retention times. One of the compounds is the same reducible one found in the other regeneration runs. The other is produced while thiobutane, RT=810, is depleted and then remains at a constant concentration. Its resistance to hydrogen reduction, along with its retention time being equal to that of a component found in butane lighter gas, implies that it is isobutane. The molybdenum catalyst may cause a rearrangement of a methyl

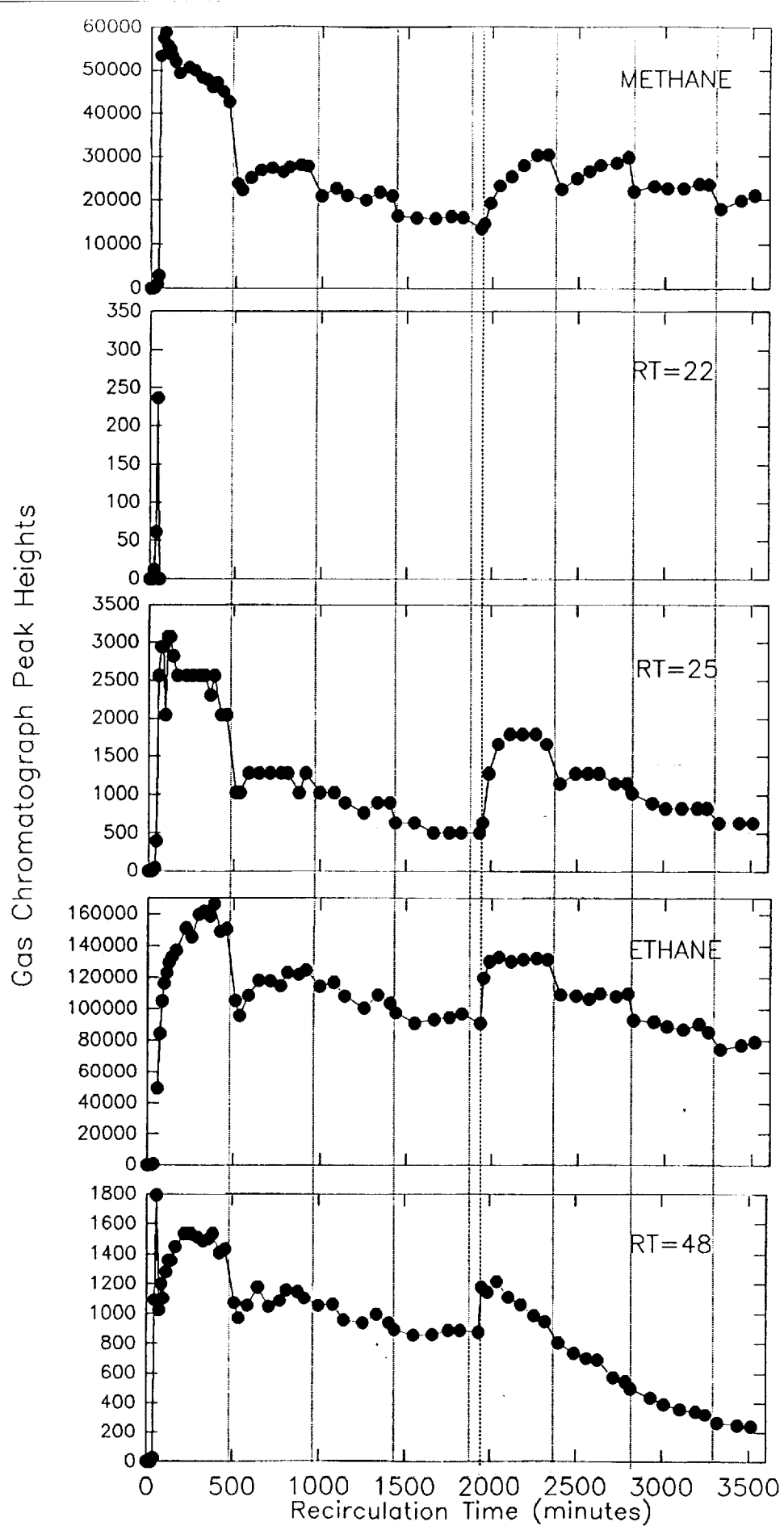


Figure 18. Final Test Stand's Fourth Regeneration Run

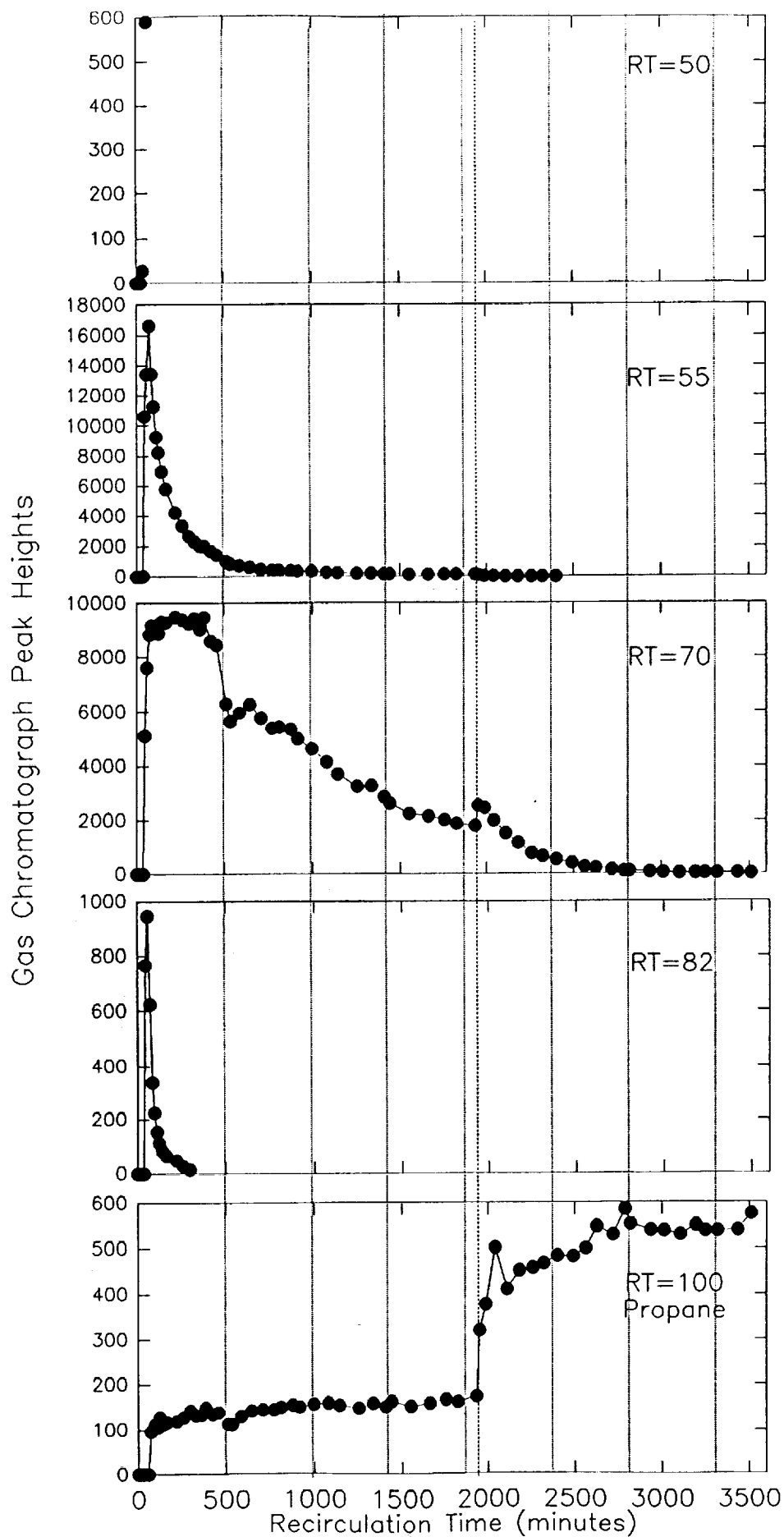


Figure 19. Final Test Stand's Fourth Regeneration Run

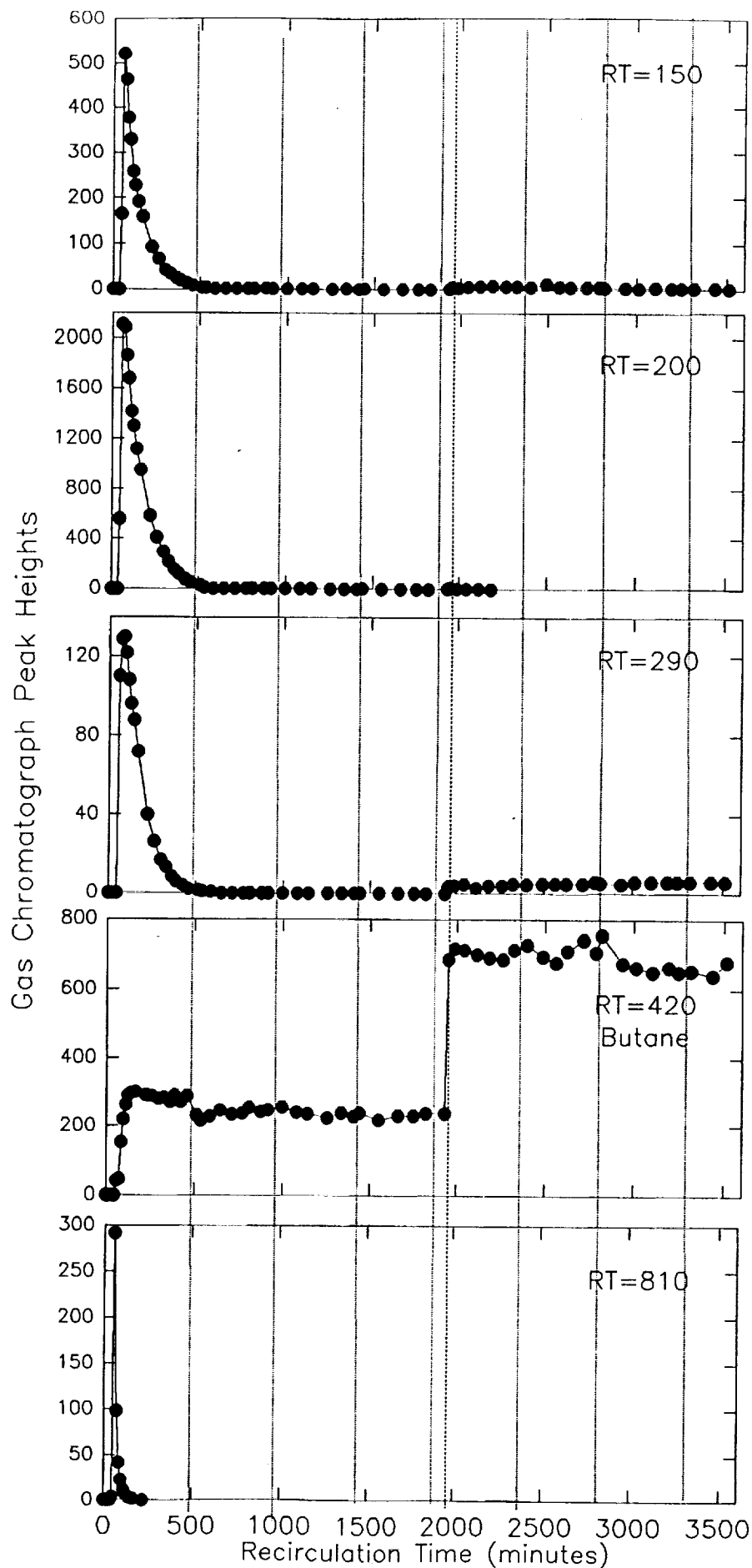


Figure 20. Final Test Stand's Fourth Regeneration Run



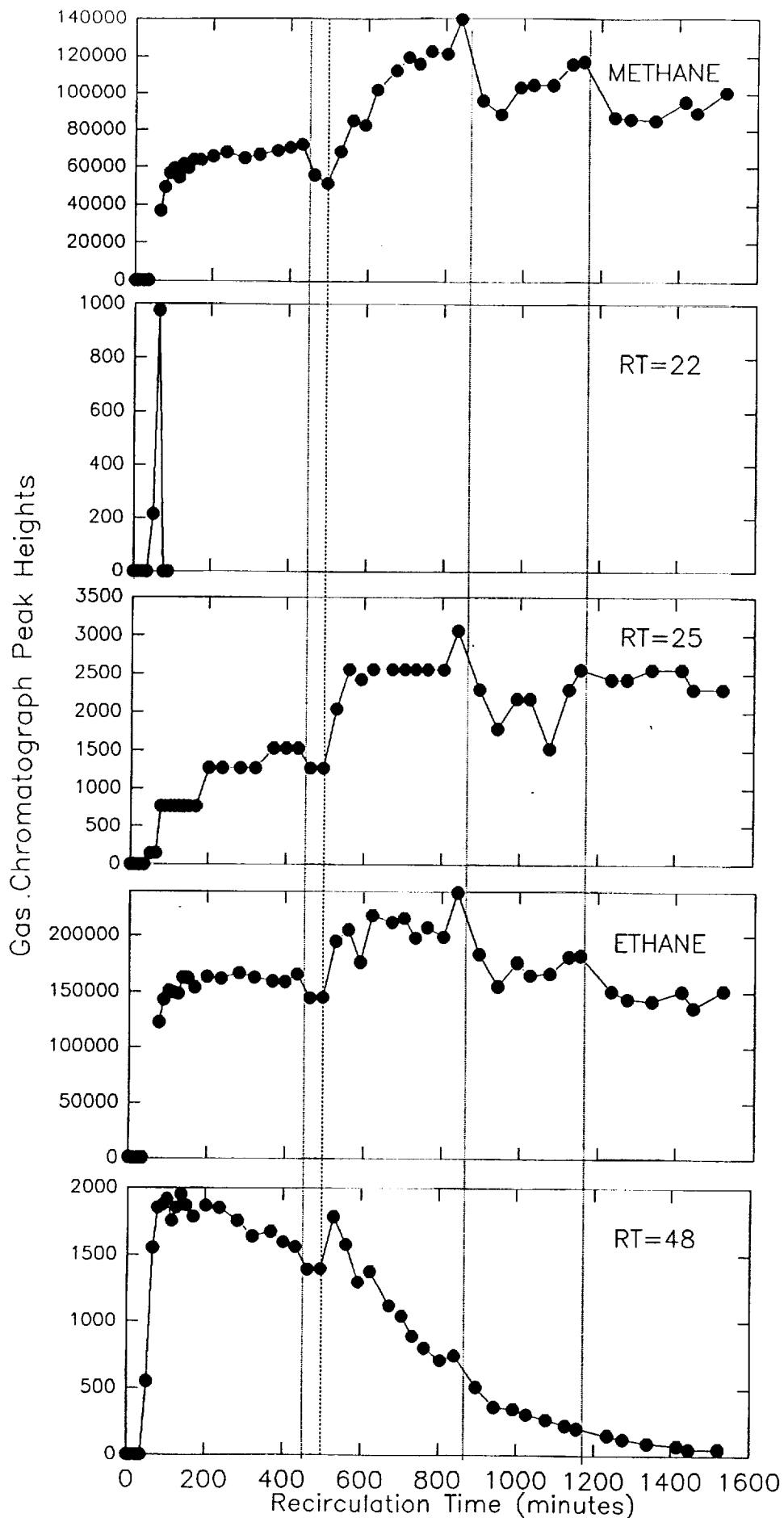


Figure 21. Final Test Stand's Regeneration Run Using the Baseline/Molybdenum Catalyst

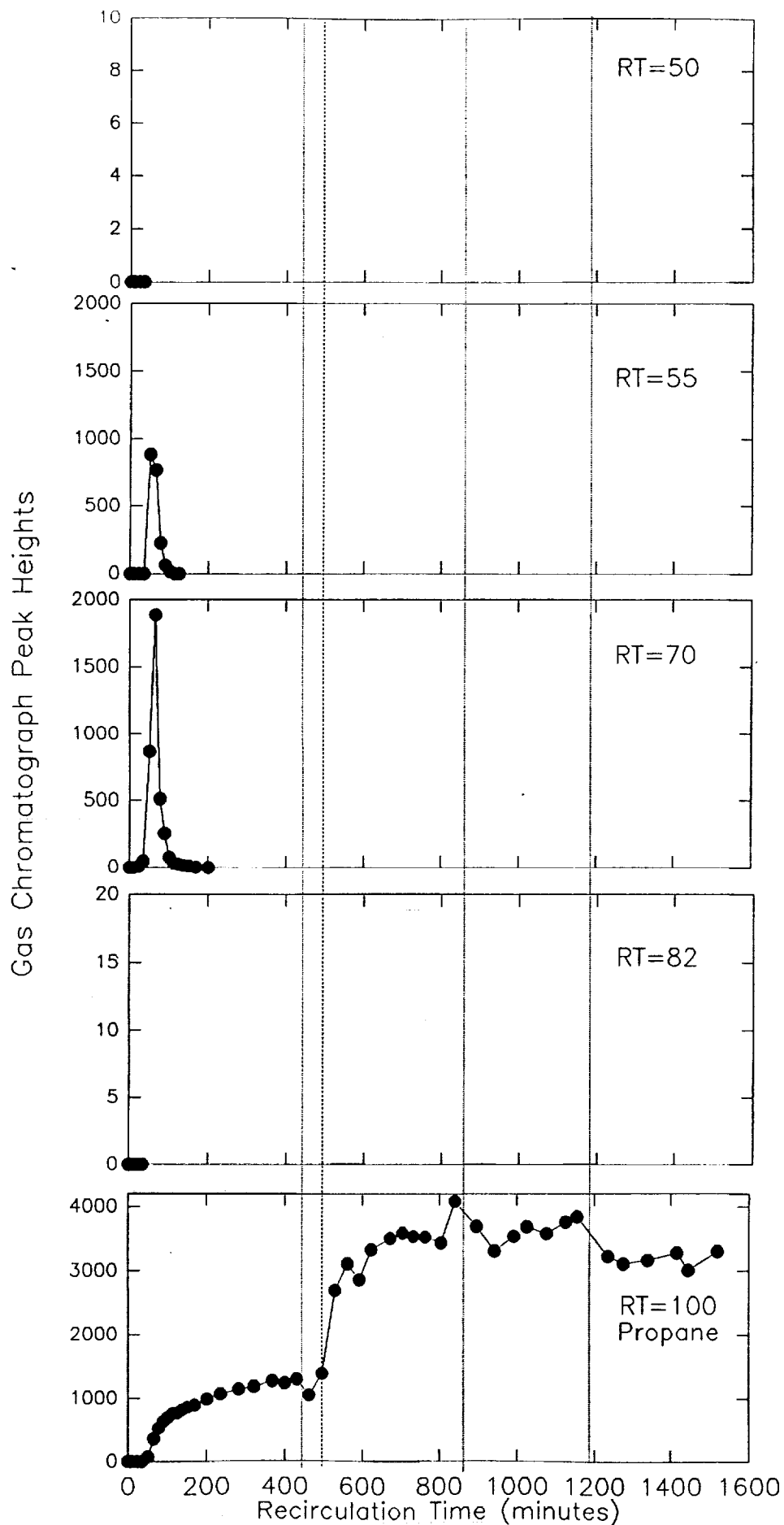


Figure 22. Final Test Stand's Regeneration Run Using the Baseline/Molybdenum Catalyst

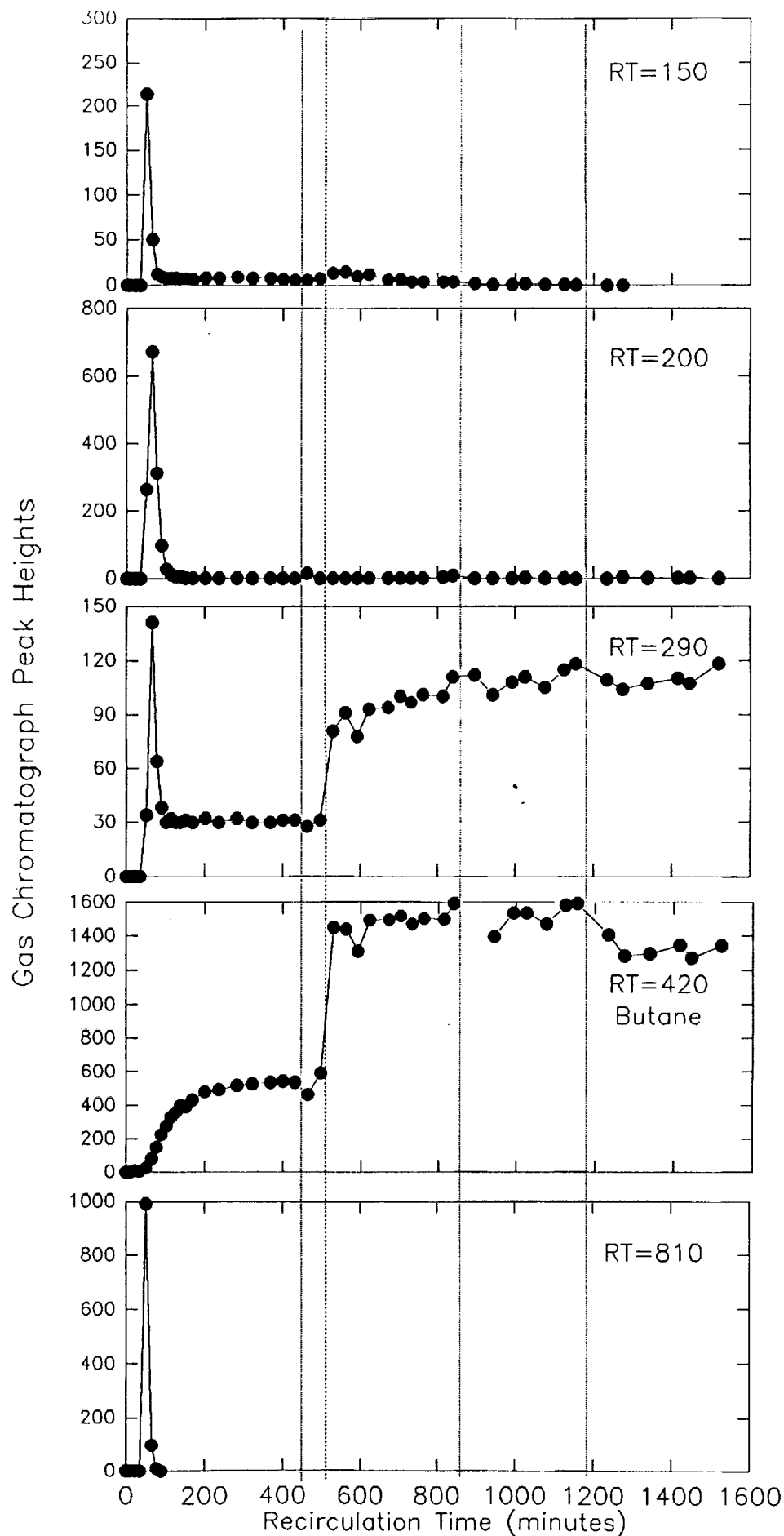


Figure 23. Final Test Stand's Regeneration Run Using the Baseline/Molybdenum Catalyst

group to the center of the carbon chain during reduction.

At 500 minutes, the temperature was raised to 300 C. As previously observed, all remaining contaminants increased in concentration in the gas stream. By 1600 minutes almost all of the reducible components were destroyed. A mechanical failure precluded the total reduction of RT=48.

## **6.0 TEMPERATURE, HYDROGEN PRESSURE, AND PRESSURE DEPENDENCE FOR THE REACTION OF DICHLOROMETHANE OVER 5% RU, 20% PT CATALYST**

The kinetic factors which determine the reaction rates during regeneration of a CARS bed include temperature, the hydrogen partial pressure, and the concentration of the contaminant. For contaminants such as Freon-113 which are hydrogenated in multiple steps, a kinetic analysis requires a detailed consideration of the sequential reactions which are involved in the complete hydrogenation reaction. Such an analysis is complex and must consider not only the catalytic surface reactions but also the competition for surface catalytic sites from the various species present in the gas phase. Such an investigation is beyond the scope of the present study. In order to gather preliminary kinetic information on a relatively simple hydrogenation reaction, dichloromethane's reaction rate as a function of concentration, hydrogen pressure, and temperature was determined.

Using the fixed bed reactor system previously shown in Figure 5, the temperature dependence of rate of dichloromethane disappearance was determined. The reactor was challenged at three different temperatures (125 C, 150 C, and 200 C) with increasing concentrations of dichloromethane until breakthrough occurred. The breakthrough concentration is dependent on the reaction rate and the catalyst bed size which is constant, and if all catalytic sites are assumed to be saturated at breakthrough, represents the reaction rate. A plot of the logarithm of the breakthrough concentration versus reciprocal temperature is shown in Figure 24. The activation energy calculated for this Arrhenius plot is 51.5 KJ/mole (12.3 Kcal/mole). Using this activation energy increasing the temperature from 125 C to 250 C will increase the reaction rate ~41 times.

The determination of the dependence of the reaction rate on the dichloromethane concentration also assumes that all catalytic sites in the CARS bed are saturated. The reaction conditions including temperature, hydrogen pressure, and flow rates were held constant. A plot of the dichloromethane concentration versus reaction rate is shown in Figure 25. All data for this plot was recorded well after breakthrough of dichloromethane had

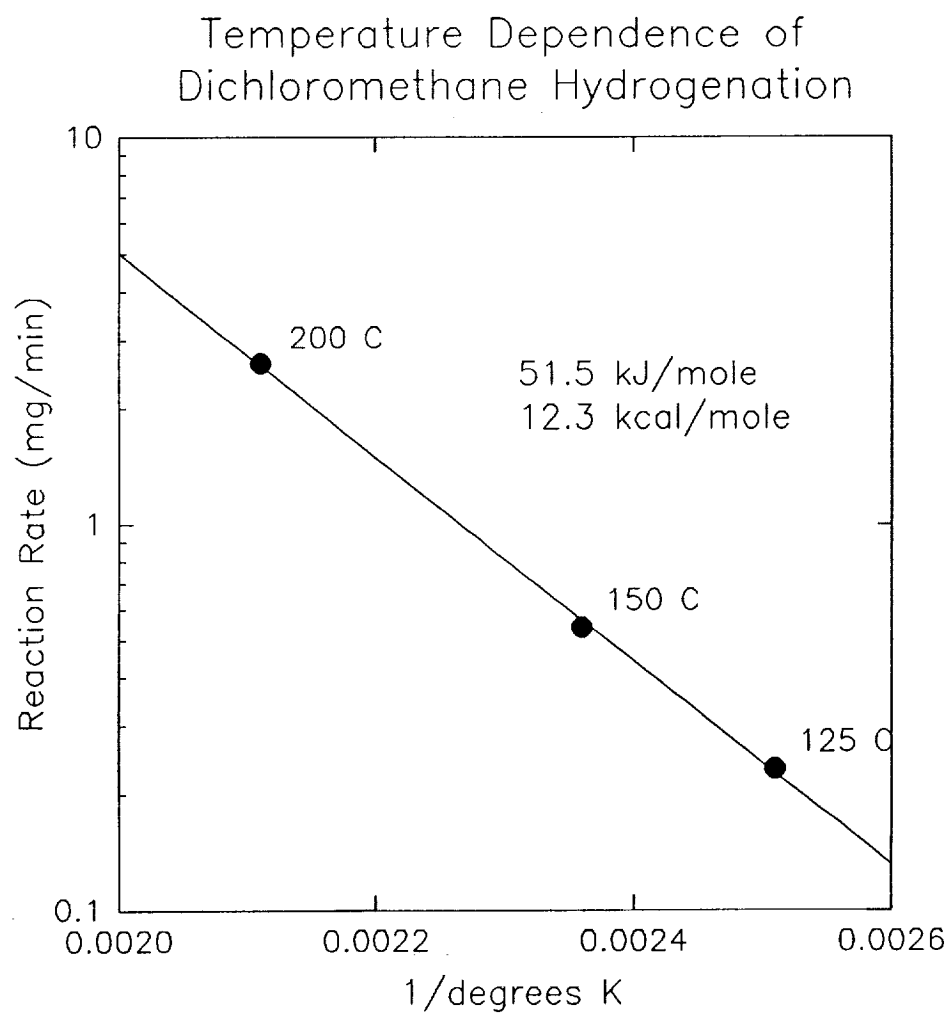


Figure 24. Temperature Dependence of Dichloromethane Hydrogenation

First Order Relationship of Dichloromethane  
to the Reaction Rate at 125 Degrees C and  
a 1.5 Minute Contact Time

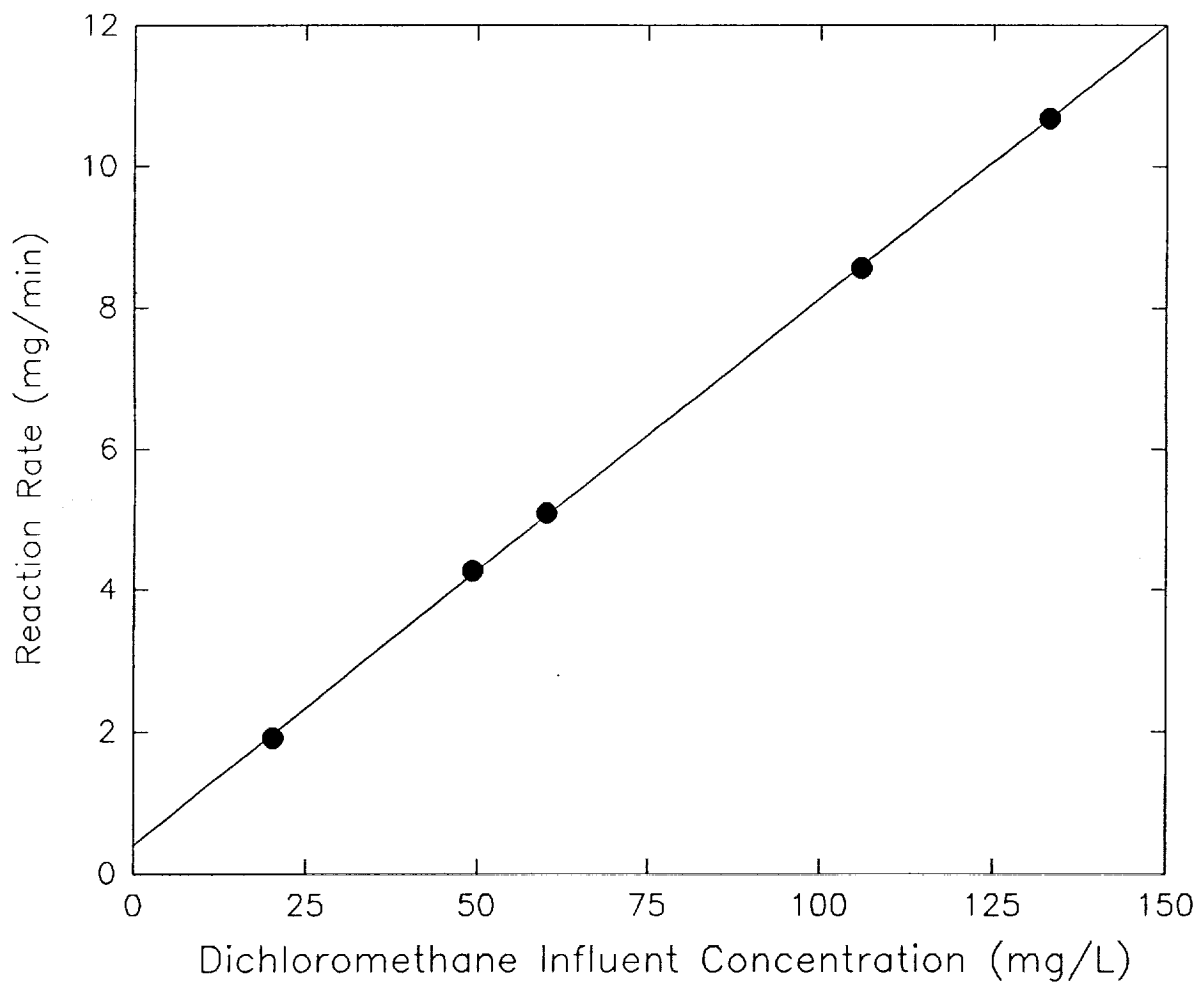


Figure 25. First Order Relationship of Dichloromethane  
to Reaction Rate

occurred. The slope indicates a linear dependence on the dichloromethane concentration. In general during regeneration, this information means that a CARS bed will initially see high reaction rates due to the high concentrations of desorbed contaminants. As the regeneration proceeds, the reaction rate will decline, and at some point a decision is made to stop based upon the time required for further regeneration relative to the current regenerated sorption capacity.

The hydrogen pressure was varied between 0.08 and 1.00 atmospheres with a constant influent level of dichloromethane. The system was maintained at 1 atmosphere with nitrogen used as the dilution gas. A plot of the reaction rate versus the hydrogen concentration is shown in Figure 26. At higher concentrations of hydrogen, the curve gives a nearly linear relation between hydrogen pressure and reaction rate; however, as the hydrogen pressure is lowered the curve bends over giving lower reaction rates than expected. The curvature of this plot is most likely due to competition for adsorption site between nitrogen and hydrogen which depresses the reaction rate at lower hydrogen pressures. The reaction rates for regeneration can be increased by raising the hydrogen pressure within those limits imposed by competitive adsorption from the contaminant species. Since hydrogen adsorbs very poorly, its pressure can likely be raised several orders of magnitude before it can effectively compete for adsorption sites with a species such as trichloroethylene.

## 7.0 CONCLUSION

The feasibility of a Catalytically Active Regenerable Sorbent (CARS) with non-catalytic sorbent additions that adsorbs problematic airborne contaminants containing hydrogen and sulfur, and then chemically converts them to more readily treatable by-products during regeneration has been demonstrated in this study. This assertion is based on analysis of adsorption, thermal desorption, catalytic hydrogenation, and regeneration data. The contaminants tested include Freon-113, trichloroethylene, bromotrifluoromethane, dichloromethane, and thiophene. Individual adsorption data for these compounds indicated that the more volatile constituents of the mixture, dichloromethane and bromotrifluoromethane, sorbed poorly on the baseline CARS. This problem was overcome by the addition of a non-catalytic sorbent, Carbosieve, which is tailored to sorb such low molecular weight highly volatile organics and which can be thermally desorbed. Thermal desorption data show that desorption of contaminants precedes the onset of high catalytic activity, and consequently, the regeneration (catalytic hydrogenation) of a CARS bed must proceed in a recirculating system where desorbed species have additional contact with the catalyst. Gas analysis by GC during

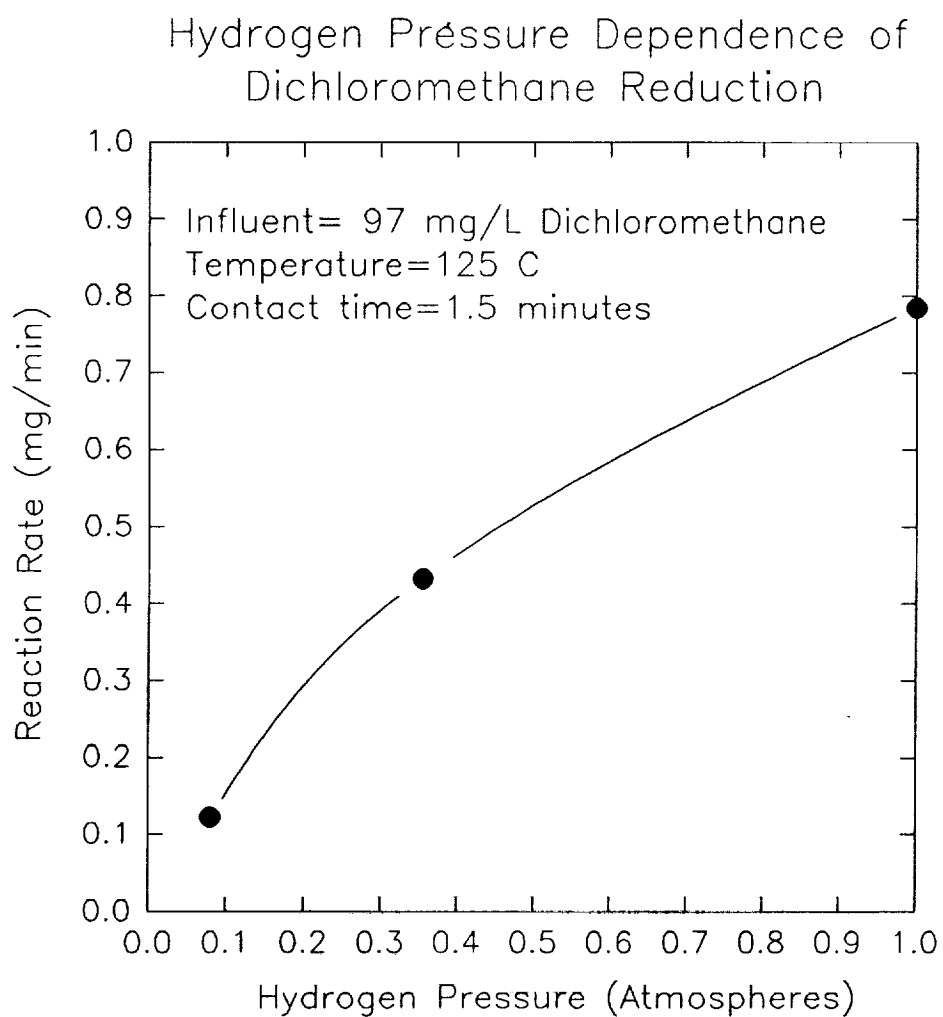


Figure 26. Hydrogen Pressure Dependence of Dichloromethane Reduction



regeneration of a CARS bed in a recirculation system proved that the hydrogenation by-products are simple alkanes. The complementary acid gases (HCl, HF, H<sub>2</sub>S, and HBr) are removed in a room temperature LiOH·H<sub>2</sub>O bed within the loop.

A complete adsorption and regeneration test performed on the best CARS combination clearly illustrates the effectiveness of this technology for the treatment of halogen and sulfur containing contaminants. The challenge mixture used contained Freon-113, trichloroethylene, bromotrifluoromethane, and dichloromethane at 436%, 15000%, 11.2%, and 95.6% of their Spacecraft Maximum Allowable Concentration (SMAC) respectively as well as thiophene, a generalized organosulfur compound without a SMAC value.<sup>1</sup> Approximately 100 liters of this challenge stream was run through a 7.8 cm<sup>3</sup> bed before breakthrough occurred. The bed was then purged, filled with H<sub>2</sub>, and heated to 250 C for 500 minutes followed by 300 C for 1100 minutes. After the initial heating during the regeneration cycle, none of the sorbed contaminants were detected demonstrating the high catalytic hydrogenation activity at these low temperatures. Subsequent GC analysis reveals the multistep hydrogenation mechanism by which more complex organics are hydrogenated. The fact that Freon-113 requires six steps for complete hydrodehalogenation slows the overall rate at which regeneration occurs. Nevertheless, after 1600 minutes the regeneration was complete and the CARS bed serviceable for a new adsorption run. This performance can be improved by increasing the hydrogen pressure and reactor temperature, and by improvements in the catalyst.

The CARS approach to remediation of problematic trace airborne contaminants can be used to replace expendable sorbent beds in the current TCCS configuration. The impact of the use of CARS in the TCCS will be lower resupply penalties, greater flexibility in handling contamination events, lower overall system weight, and possibly lower energy consumption. This last assertion is based on a projected lower catalytic oxidizer operation temperature due to an influent which is well defined consisting of known concentrations of alkanes without any catalyst poisons, and possibility of operating the catalytic oxidizer only during a regeneration. There are other potential applications of the CARS concept. The Environmental Protection Agency policies on the release of chlorofluorocarbons (CFCs) will require industry to capture, recycle, replace, or destroy their CFCs. The current list of regulated CFCs can only be expected to expand, and the need for new technologies to deal with industrial use of these chemicals will grow. The CARS technology can be used to capture relatively low concentrations of CFCs and then to destroy their harmful characteristics.

## 8.0 FUTURE WORK

The practicality of replacing expendable sorbent beds in the TCCS with a CARS system depends on its ability to load all contaminants to practical levels, and then to catalytically hydrogenate oxidation catalyst poisons without undue influence from other adsorbed species. This initial NRA project has investigated only a few of the halogenated organics composing the TCCS model. The adsorption characteristics of the other TCCS components, including those which are not oxidation catalyst poisons, must be determined in order to design a bed which will be effective against a realistic mixed stream. The effect that the presence of the other contaminants will have on the halogen reduction and separation during the regeneration phase must also be investigated.

It was shown in this investigation that the addition of molybdenum to the baseline catalyst significantly changes its catalytic characteristics. The molybdenum increased the catalysts effectiveness but caused it to produce elemental carbon. The effects from adding other base metals to the baseline catalyst should be investigated.

At the end of a regeneration cycle, unreacted hydrogen will be present in the regeneration loop. Methods using a regenerable metal hydride bed should be investigated which will release hydrogen into the regeneration loop when needed and will readsorb the excess hydrogen at the end of a regeneration run.

A method for detecting the breakthrough of halogenated organics as a class of compounds must be developed to determine when a regeneration is necessary. The most promising method would be that of using an infrared adsorption system tuned to those frequencies indicative of a carbon chlorine or carbon fluorine bond. A similar detector could be used to determine when catalytic regeneration is complete.

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## 13. ABSTRACT (Maximum 200 words)

Thermally regenerable sorbent beds have been demonstrated to be a highly efficient means for removal of toxic airborne trace organic contaminants aboard spacecraft. The utilization of the intrinsic weight savings available through this technology has not been realized since many of the contaminants desorbed during thermal regeneration are poisons to the catalytic oxidizer or form highly toxic oxidation by-products in the Trace Contaminant Control System (TCCS). Included in this class of compounds are nitrogen, sulfur, silicon, and halogen containing organics. The catalytic reduction of these problematic contaminants using hydrogen at low temperatures (200-300 C) offers an attractive route for their destruction since the by-products of such reactions, hydrocarbons and inorganic gases, are easily removed by existing technology. In addition, the catalytic oxidizer can be operated more efficiently due to the absence of potential poisons, and any posttreatment beds can be reduced in size. The incorporation of the catalyst within the sorbent bed further improves the system's efficiency. The demonstration of this technology provides the basis for an efficient regenerable TCCS for future NASA missions and can be used in more conventional settings to efficiently remove environmental pollutants.

## 14. SUBJECT TERMS

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